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Effect of pH and exchangeable metals on phosphate adsorption by soils

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Effect of pH and exchangeable metals on phosphate adsorption by soils

by

Ibrahim Bakry Abdul Razaq

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TABLE OF CONTENTS

INTRODUCTION

The reaction between phosphorus (P) and soils has been under intensive investigation since the early years of this century. Therefore, it is the most frequently studied subject in soil science. The importance of P in plant nutrition, the widespread occurrence of phosphate deficiency, and the complex nature of the reactions of phosphate in soils are the main reasons for the extensive work on this element. It is well known that the major portion of P fertilizers added to soils enter the solid phase as adsorbed or precipitated forms. The high surface areas of most soils and the rapidity of adsorption reaction suggested that phosphate behavior in soils is controlled mainly by adsorption processes, which are important mechanisms in controlling phosphate in soil solution.

Although phosphate adsorbed to soil solids is in equilibrium with soil solution, this equilibrium is not as simple as it may seem because it is affected by various factors operating simultaneously. Among these factors, pH, concentration of electrolytes in solution, period of reaction time, and other soil properties such as clay and organic matter contents are the most important.

Although pH is one of the most dominant factors affecting phosphate adsorption by soils, little information is available about the relationship between phosphate adsorption and pH values of specific soils. When the pH values and phosphate adsorption of many soils are considered, this relationship is masked by the variation of other soil properties.

This may be the reason why many authors have failed to obtain a significant correlation between phosphate adsorption and soil pH. Moreover, conflicting reports are found in the literature on the effect of liming (adjusting the soil pH by adding $CaCO_3$) on phosphate adsorption.

The effect of neutral salts on phosphate adsorption has been the subject of numerous studies, but information on exchangeable metals in soils on phosphate adsorption is scarce. Recent studies, however, have produced evidence that the equilibrium between surface adsorbed phosphate and phosphate concentration in solution is influenced to a considerable degree by the nature of the exchangeable cations. Therefore, the role of exchangeable cations in phosphate adsorption by soils deserves investigation.

Therefore, the objectives of this study were: (1) to develop a simple method for determination of surface charge density of soils; (2) to assess the effect of pH on phosphate adsorption by slightly acid soils; (3) to assess the effects of leaching and ammonium saturation on phosphate adsorption by soils; (4) to assess the effects of exchangeable alkali, alkaline earth, and selected heavy metals on phosphate adsorption by soils; and (5) to assess the effect of matrix solution on phosphate adsorption by soils using kinetic models.

LITERATURE REVIEW

The phosphorus (P) content of the earth's crust is approximately 0.12%. Although soils, rock, natural water, and biomass contain P, the level of P in the atmosphere and in precipitation is extremely low (Tabatabai et al., 1981). Inorganic and organic soil phosphate may have an important role in supplying P to growing plants (Anderson, 1980). However, the equilibrium state between labile and nonlabile P takes a long time to reestablish, when labile phosphate is diminished, because of very low solubility of soil phosphate compounds (Ulrich and Khanna, 1968; Chang and Jackson, 1957). Therefore, phosphate fertilizers are applied to soils to supplement the plant available P.

The recovery of fertilizer P by crops amounts to only 10 to 30% of the quantity added to soils. The remaining 70 to 90% is assumed to be consumed by precipitation and adsorption by the soil constituents. Initially, a considerable portion of the applied P is available to plants and then decrease with time. The reaction rate of P with soil minerals is a function of phosphate concentration, and the total amount reacted is a function of time (Russell and Prescott, 1916).

The high initial rate of reaction of phosphate is usually followed by slow reaction which causes a slow decline in the concentration of phosphate in soil solution (Munns and Fox, 1976). Barrow and Shaw (1975) represented all the reactions of soil phosphate as a three compartment system: A=B=C, where A represents phosphate in solution; B the adsorbed phosphate; and C, phosphate which has been converted into

a form which is not in direct equilibrium with phosphate in A. Therefore, adsorbed phosphate is the major source for plant-available P. It is well known that adsorption is a very important phenomenon in the chemistry of soil P and is one mechanism which determines the P concentration in soil solution.

The phosphate adsorption reactions are affected by numerous factors operating simultaneously (Parfitt, 1978; Barrow, 1985). These factors include pH, type and concentration of electrolytes, clay content, Al and Fe oxides, exchangeable cations, and organic matter content. Of the factors mentioned above, those pertaining to this study will be discussed in more detail in the following sections.

Effect of pH on Phosphate Adsorption by Soils

The pH of the soil is probably the most important operating factor affecting the P adsorption by soils. The important effect of pH on phosphate adsorption may be related to the fact that the pH of the solution has a major effect in determining the phosphate ionic form, which in turn determines its reactivity in soils. Thus, the relative amounts of the three phosphate species ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) are governed by the pH of the ambient solution. The pK_1 and pK_2 of the H_3PO_4 occur at pH values of 2 and 7, respectively. Consequently, these two ionic forms are the most important in agricultural soils. However, HPO_4^{2-} with two nucleophilic centers and the potential to act as a bidintate ligand may have a far greater affinity for the surface than $H_2PO_4^-$ (Parfitt et al., 1975; Bowden et al., 1980b). The adsorption

of P as HPO_4^{2-} rather than $H_2PO_4^-$ has also been reported for phosphate adsorption by a variable-charge mineral surface (Bowden et al., 1980a). Moreover, Taylor and Ellis (1978) investigated a mechanism of phosphate adsorption on soil and anion exchange resin surfaces and reported that pH values of the equilibrium phosphate solutions suggested that there was deprotonation of $H_2PO_4^-$ ion during initial stages of adsorption. They also concluded that, at low concentrations, phosphate was bonded by two points of attachment after deprotonation of the $H_2PO_4^-$ ion, followed by one point of attachment at higher phosphate concentrations during adsorption on resin surfaces.

Two interacting factors influence phosphate adsorption by charged surfaces as the pH increases from 2 to 7. Firstly, as the pH increases, the concentration of divalent HPO_4^{2-} ion increases ten fold for each unit in pH (Lindsay, 1979). Secondly, the surface becomes increasingly negative as the pH increases, resulting in greater electrostatic repulsion. However, the increase in HPO_4^{2-} concentration offsets the decrease in electrostatic potential with the increase in pH (Bowden et al., 1980a). Thus, phosphate adsorption by goethite and amorphous hydroxyl Al surfaces decreases relatively slowly until the pK_2 of H_3PO_4 is reached at pH 7 (Bowden et al., 1980a; Kwong et al., 1979b). Above pH 7 the increase in concentration of the divalent ions slows to zero, whereas the decrease in surface potential continues. This may be the reason for the fast decrease in ion adsorption which has been observed for phosphate and other anions by Hingston et al. (1967, 1972) for

synthetic variable charge surfaces as the pH increases. They concluded that, at pH values where the H_3PO_4 is fully dissociated (pK_2), specific adsorption occurs only to the extent of the positive charge of the surface. In addition to that, little specific adsorption is found at pH values more alkaline than the zero point of charge (zpc), providing the pH is somewhere near a pK_a value of the acid, where the energy required to abstract a proton from the acid is at a minimum (Hingston et al., 1972).

Hydrogen ion activity (pH) may also influence the net charge in plane of adsorption in soils with variable charge colloids. The sign and magnitude of the surface charge of these colloids depend on the pH (Van Raij and Peech, 1972; Bell and Gillman, 1978). Due to the amphoteric behavior of these colloids, their variable charge depends on the H^+ ion concentration in the ambient solution and becomes increasingly negative as the pH increases (Bowden et al., 1980b). In general, there are two lines of evidence on the effect of pH on phosphate adsorption by the variable charge surfaces. The first suggests that phosphate adsorption is the greatest at the lowest pH. This may depend on the net increase in positive charge on the surfaces with the decrease in the pH value. This was confirmed by the finding that the maximum phosphate adsorption on such surfaces occurs at slightly below pH 4 (Parfitt, 1978). Also by the findings of Bolan et al. (1986), who reported that, for two surface soils of contrasting mineralogy, adsorption of phosphate decreased with increasing pH above 4. Earlier,

Deb and Datta (1967a,b) found that the highest phosphate adsorption by soil occurred at pH 4. They attributed this to the high activity of Fe and Al which was accompanied by development of positive charge in soil colloids. However, the low retention at high pH was attributed to the decrease in Fe and Al activities and the decrease in positive charges on colloidal surfaces. Cabrera et al. (1981) explained the larger amount of slowly exchangeable P at pH 3.5 than at pH 7.0, for phosphated lepidocrocites, on the basis of electrical charge developed by the oxide surfaces in solution. At pH 7 (close to the zpc) surface charge is low, so phosphate ions are expected to be adsorbed with difficulty.

The second line of evidence suggests that there is a pH at which phosphate adsorption is at a minimum and it increases on either side of this pH. Murrmann and Peech (1969) found that for any given soil the amount of labile phosphate and phosphate concentration in soil solution reached a minimum value at about pH 5.5 and increased rapidly as the pH was either increased or decreased from this value by the addition of HCl or $Ca(OH)_2$. For acidic soil of pH 3.8 limed to pH 7, Amarasiri and Olsen (1973) found that labile and soluble phosphate decreased to minima at a pH between 6 and 7. The decrease in concentration of phosphate in soil solution with increase in pH has been demonstrated in a number of soils (MoKwunye, 1975; White and Taylor, 1977). Haynes (1982), in reviewing the effects of liming on P availability, concluded that as the pH increases the phosphate concentration in soil solution is generally observed to firstly decrease, pass through minimum, and then increase.

Conflicting reports, however, are found in the literature on the effect of pH on phosphate adsorption, especially when liming is used as a practice to adjust soil pH. In a recent review, Sanchez and Uehara (1980) concluded that a considerable controversy exists in the literature regarding whether or not liming decreases phosphate fixation. Also, in another review, Probert (1980) concluded that reports on the effect of liming on the adsorption of phosphate are conflicting; for example, adsorption has been shown to be increased, decreased, or unaffected by liming soils. Also, liming has been reported to increase, decrease, or not affect the phosphate that can be extracted from soils (Haynes, 1982).

These controversial reports on the effect of pH (by liming) on phosphate adsorption by soils may be related to the fact that pH is not affecting the phosphate ion forms alone but also several other factors. These other factors may play a major role in phosphate adsorption by soils (Barrow, 1984). These include: (1) the differences in mineralization of organic P in limed and unlimed soils. Haynes (1982) suggested that increasing soil pH may increase the rate of mineralization of organic P and different soils differ in their organic P contents. (2) Increasing soil pH will precipitate exchangeable Al as a polymeric compound of very effective adsorption sites (McLean, 1976; Sims and Ellis, 1983). White (1983) has criticized some aspect of this suggestion but supported the general idea by suggesting that differences between soils in the effects of pH arise because soils differ in their

exchangeable Al. This factor will be discussed in more detail under the effect of exchangeable Al on phosphate adsorption by soils. (3) The release of phosphate from the soil itself, which is influenced by pH, affects its adsorption by soil. Barrow (1984) found that the release of P was most marked at low pH when six soils were incubated at 60°C with several levels of either $CaCO_3$ or HCl. A simple explanation for this effect, as was given by Barrow (1984), is that acidity decomposed some of the phosphate-retaining material in soils. (4) The final factor influencing the effect of pH on the retention of phosphate is the ionic medium in which adsorption is measured. At a surface of positive charge, a decrease in ionic strength makes the electrostatic potential in the plane of adsorption more positive, consequently decreasing the retention of cations by increasing retention of phosphate. However, at a negatively charged surface, a decrease in the ionic strength makes the potential more negative, thus decreasing retention of phosphate (Barrow et al., 1980b). This factor will be covered in more detail under the topic of effect of ions in solution on phosphate adsorption by soils.

Effect of Al and Fe Oxides and Exchangeable Al on Phosphate Adsorption by Soils

Oxide and hydrated oxide surfaces of Al and Fe play a major role in phosphate adsorption in acid and neutral soils (Bromfield, 1965; Syers et al., 1971; Torrent, 1987; Lopez-Hernandez and Burnham, 1974a,b). Aluminum and Fe oxides usually exist in soils as discrete

compounds, as coatings on soil particles, or as amorphous Al or Fe hydroxyl compounds (Sample et al., 1980). Studies with an electron microscope by Fordham and Norrish (1974, 1979) suggested that Fe oxides, and especially goethite, are very important in phosphate adsorption in soils.

Surface adsorption and precipitation are two processes commonly employed in the interpretation of mechanism of phosphate fixation by Al and Fe oxides and clay minerals. However, Wild (1953) suggested the adsorption process to be the most important mechanism, because there is normally not enough Fe and Al ions in soil solution to precipitate a significant amount of P, which is usually immobilized in a relatively short time.

As White and Taylor (1977) pointed out, although surface adsorption theories may describe the way in which the phosphate concentration in the soil solution responds to the amount present in the solid phase, they fail to account for the way in which the amount of adsorbed phosphate accessible to isotope exchange varies in response to soil pH. In contrast to this process, theories based upon the formation of crystalline compounds (precipitation) do not readily lead to prediction of variations in soil solution concentration. However, using chemical thermodynamic concepts to distinguish adsorption from precipitation for aluminum-phosphate interaction, Miller et al. (1986) found that this interaction is conducive to adsorption rather than precipitation.

More than one mechanism has been proposed to describe the phosphate adsorption in soils by Al and Fe oxides. Depending on reaction of

phosphate and Al and Fe hydrous oxides in buffers of 0.1 M ionic strength, Bache (1964) showed three stages to the reaction: (1) a high energy chemisorption of small amounts of phosphate, (2) precipitation of a separate phase of phosphate, and (3) a low energy adsorption of phosphate onto the precipitate. Bache (1964) concluded that a high-energy chemisorption of small amounts of phosphate by both Al and Fe hydrous oxides occurs over a wide pH range without precipitating Al^{3+} and Fe^{3+} ions; with larger amounts of phosphate, Al^{3+} and Fe^{3+} ions are precipitated as insoluble phosphate. When the activity of these ions are reduced to very low values, the increasing addition of phosphate is adsorbed at low energy, which may be physical adsorption onto a phosphate-saturated surface or may replace phosphate ions which diffuse into the solid. The composition of the precipitated products are likely to be

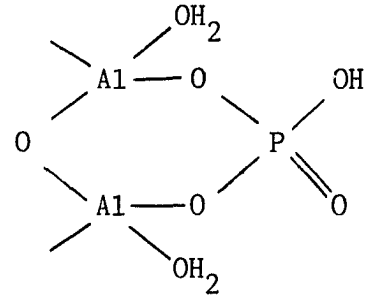
$$(Al,Fe)(H_2PO_4)_n(OH)_{3-n} ,$$

where n=1 at pH values below 3.5 for the Al system and below 1.5 for the Fe system but is <1 at higher pH values (Bache, 1963).

Three stages mechanism was also suggested for phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite, depending on adsorption isotherms at pH values ranging from 3 to 10 (Muljadi et al., 1966a,b). These three regions are related to the affinity of phosphate for three energetically different sites. Muljadi et al. (1966a,b) found that the mechanism for phosphate adsorption in regions I and II was the exchange of phosphate for OH^- groups associated with Al atoms. In region I, the

phosphate concentration is $<10^{-4}$ M, and adsorption with a very high affinity takes place by exchange of phosphate with one OH^- group. In region II, the phosphate concentration is approximately 10^{-4} M, and the second OH^- group is involved. Al ions are thought to be derived from the edge surface of the crystal mineral involved (Cashen, 1959). Adsorption in region III, at phosphate concentration from 10^{-3} to 10^{-1} M, is associated with some clay minerals less crystalline than the bulk minerals. Phosphate adsorbed in region II and III of the hydrous oxide becomes less reversible with increasing pH.

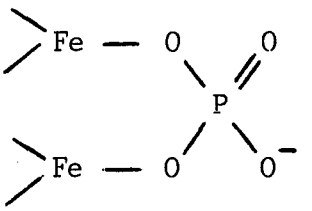
Other studies have shown that phosphate held as monodentate ligand at the edge of the crystal becomes tightly bonded with a slight rise in pH due to the formation of a bridging ligand (Kafkafi et al., 1967):



Other work by Murrmann and Peech (1969) showed that the stability of such a ring structure should be at maximum around pH 6. Subsequently, Kyle et al. (1975) showed that the rate of isotopic exchange of phosphate adsorbed on gibbsite is the slowest between pH 5 and 6, which they attributed to the formation of the ligand structure at the edge faces of the gibbsite crystals.

The theories of Hingston et al. (1967, 1968) describe the phosphate adsorption by oxides and promote the specific adsorption mechanism of phosphate ions by soils. The specific adsorption mechanism involves the presence, in solution, of HPO_4^{2-} ions, which are able to form coordinated links with metal ions such as Fe^{3+} or Al^{3+}, and ions other than hydrogen (e.g., $H_2PO_4^-$), which are able to donate a proton to the surface. Such kind of adsorption is also called ligand adsorption (Hingston et al., 1974). The specific adsorption reaction also involves adsorption of phosphate and other incompletely dissociated acids. This can take place at pH values more alkaline than zpc provided the pH is somewhere near a pK_1 value of the acid, and where the energy required to abstract a proton from the acid is a minimum (Hingston et al., 1972, 1974). Thus, phosphate was suggested to exchange with OH_2 and OH associated with Fe or Al at the edge of the crystal and becoming coordinated to the metal ion at the surface and specifically adsorbed. Hingston et al. (1967, 1968) showed that when anions are specifically adsorbed they take up protons from either the oxide surface at pH values below the isoelectric point or from the dissociation of the acid itself when the charge on the oxide is negative. This lower average negative charge of the anion permits a coordinate link to be formed with the metallic ion. As a consequence of this, the net charge on the surface becomes more negative and the pH of the solution increases. This suggested mechanism of phosphate adsorption is therefore different from those described by Bache (1964) and Muljadi et al. (1966a,b) who thought that phosphate ions replaced hydroxyl ions only.

By using isotopic exchange technique, Atkinson et al. (1972) also confirmed the bidentate binding of some of the phosphate. They found that the lability of phosphate adsorbed on oxide surfaces depends on the formation of ring structures. Binuclear bridging was also suggested as a mechanism for the adsorption process on synthetic Fe oxide when pairs of Fe-OH react with phosphate (Parfitt et al., 1975, 1976). Also, Parfitt (1977) reported that phosphate reacts with FeOH and $FeOH_2^+$ groups on Fe oxide surfaces to form a binuclear bridging $FeOP(O_2)OFe$ complex as:



and with exposed $Al(OH)H_2O$ on kaolinite edges and on hydroxy Al species to form a binuclear or bidentate phosphate complex.

In addition to the importance of Al and Fe oxides for phosphate adsorption by soils, freshly precipitated hydroxy-Al and -Fe cation polymers have a marked effect on phosphate adsorption. Haynes (1983) found that liming a Spodosol soil, initially high in exchangeable Al, resulted in formation of new highly active adsorbing surfaces due to the precipitation of exchangeable Al as amorphous hydroxy-Al cations. Phosphate adsorption greatly increased by the formation of these newly formed surfaces. However, Haynes (1983) found that air-drying after

liming increased the adsorption due to the crystallization of amorphous hydroxy-Al compound. McLean (1976) reported the formation of more insoluble hydroxy-Al species as the soil pH increased into the range of minimum solubility of Al ion in soils. These hydroxy-Al species include a large range of positively charged polynuclear complexes as well as a series of polymers with formula $Al(Al_2(OH)_5)_n^{3+n}$.

Rengasmy and Oades (1978) found that in Al solutions molecular weight of the polycations formed depend on the OH/Al ratio. When the ratio was <2.0, the polycations formed had molecular weight <50,000, high positive charge, and did not condense to a solid phase over 6 months. However, when the ratio was above 2, the polycation had molecular weight >100,000, low positive charge, and rapidly condensed to a solid phase with a cyclic structure. Rengasmy and Oades (1979) suggested that polycations can be formed by bridging of Al(III) and Fe(III) through hydroxyl groups. Haynes (1983) concluded that interaction of polymeric hydroxy species with clay minerals can change the physiochemical properties of colloids.

Sims and Ellis (1983) examined P adsorption by "pure" Al-OH suspensions as a function of pH of Al-OH precipitation, length of incubation, and ionic strength. They found that aging of Al-OH suspensions reduced their capacity for phosphate adsorption, and that Al-OH precipitated at pH 5.5 initially adsorbed more P than that precipitated at pH 7.0, the difference becomes insignificant within 90 days. The Al-OH fraction in highly weathered acidic soils have widely

varying capacities to adsorb phosphate, depending on the degree of polymerization/crystallization of the compounds. Perrot et al. (1974) have shown that hydroxyl-Al species are readily adsorbed onto negative charged surfaces and in turn adsorb P. Colemena et al. (1960) and Hall and Baker (1971) found that the adsorption of P by soils and other materials with predominantly constant-charge surfaces increases with increases in the percent neutralization of the exchangeable Al and Fe. But the role of exchangeable Al, Fe, and other metals in soils in phosphate adsorption is not fully understood and deserves investigation.

Effect of Ionic Strength and Ions in Solution on Phosphate Adsorption by Soils

Many studies have shown that phosphate adsorption by soils varies with the nature of the ionic composition and the ionic strength of the supporting matrix solution (Helyar et al., 1976a; Robarge and Corey, 1979). It has been shown that increasing the concentration of nitrate and chloride salts of Ca, Mg, Na, K, and NH_4 increases the adsorption of phosphate by aqueous suspensions of soils, clay, and hydrous oxides of Fe and Al (Kurtz et al., 1946; Clark and Peech, 1960; Fordham, 1963; Jensen, 1970). Also, in a study designed by Sims and Ellis (1983) to investigate the change in phosphate adsorption associated with aging of Al hydroxide suspension, they showed that reducing the ionic strength of the Al-OH suspension by dialysis produced gibbsite and caused an 80-90% decrease in phosphate adsorption maxima, as calculated by the Langmuir model.

The effect of ionic strength on phosphate adsorption by variable charge surface varies depending on the pH. Barrow et al. (1980b) found that, at a pH lower than zpc, phosphate adsorption by goethite, in the presence of varying concentrations of NaCl and $CaCl_2$, decreased with an increase in the concentration of either salts. However, as the pH increased, a point was reached at which there was no effect of salts on adsorption. Beyond this point (i.e., at a pH higher than zpc), increasing the concentration of salt increased the adsorption, and the increase in adsorption was higher in the presence of $CaCl_2$ than that in the presence of NaCl. Madrid and Posner (1979) found that at pH < zpc 0.01 M NaCl as an equilibrium medium leaves more phosphate on the oxide than does 0.1 M NaCl. The opposite is true for pH values > zpc. Several explanations have been offered for the effects of salt concentration on phosphate adsorption. Upon studying the influence of neutral salts on phosphate ion concentration in soil solution, Clark and Peech (1960) found that certain cation activity ratio and ion activity products involving Ca^{2+}, H^+, K^+, and $H_2PO_4^-$ remain constant in soil and clay suspensions as the electrolyte concentration increased. They reported that the observed constancy of the ion activity product related either to phosphate ion coadsorbed with exchangeable cations on the soil particles or the existence in the soil of a crystalline phosphate compound having a definite solubility product. As a result, an increase in Ca concentration is opposed by a decrease in phosphate concentration. This explanation does not seem practical because it requires that the soil

cation-exchange capacity to be so large that the concentrations of exchangeable cations are almost independent of changes in electrolyte concentration (Barrow, 1972). This seems not to be possible, and therefore the resulting ion products are not constant.

Studying the influence of the ionic strength and cation species of the matrix solution on phosphate adsorption by four contrasting unfertilized soils, Ryden and Syers (1975) found that an increase in ionic strength enhanced phosphate adsorption during the first 40 h and that the cation species influenced the amount of phosphate adsorbed, as shown by the isotherms obtained in 10^{-2} M Ca and $3x10^{-2}$ M Na system. Although pH affected the amounts of P adsorbed, pH effects alone could not adequately explain the differences in P adsorption. Kinetic analysis of the results obtained by Ryden and Syers (1975) indicated that within the range of P addition that they used for each soil, the equilibrium P concentration, at finite time, was independent of ionic strength and cation species. Consequently, the composition of the solution affected only the rate at which equilibrium was attained. They attributed the results to the effects of ionic strength on the surface charge of retaining components and the thickness of the diffuse double layer, and the effects of specific adsorption of a divalent cation on surface charge, as they relate to the rate of P adsorption. Other studies by Barrow and Shaw (1979a,b), however, indicated that the change in phosphate concentration was not proportional to the reciprocal of time as suggested by Ryden and Syers (1975). Consequently, the validity

of extrapolation from short sections of reciprocal-time plots as proposed by Ryden and Syers (1975) in order to estimate phosphate concentration in the equilibrium solution is questioned, because it seems that it cannot be universally applied to all soils.

Another explanation for the effect of salts on phosphate adsorption was given by Helyar et al. (1976a). They investigated the effects of salts on phosphate adsorption by gibbsite at pH 5.5 and found that increasing the $CaCl_2$ concentration from 0 to 20 mM increased the adsorption of phosphate (ranging in final concentrations from 1 to 100 μM). They postulated that Ca^{2+} ions in solution increase phosphate adsorption because it complexes with the adjacent adsorbed phosphate ions and reduces the repulsion forces between them. The fact that Mg, K, and Na do not affect phosphate adsorption, whereas Ca does have an effect, suggests a specific association between Ca and the phosphate adsorbed by gibbsite (Helyar et al., 1976a). This explanation seems to contradict the early findings of Lehr and Van Wesemael (1952) and Clark and Peech (1960), which indicated that phosphate adsorption by acid soils shows a definite response not only to the ionic strength but also to cationic species of the neutral salt solutions (KCl, $NaNO_3$, $Ca(NO_3)_2$). This discrepancy of the effect of cations in solution on phosphate adsorption by soils has been explained by Helyar et al. (1976a) as follows: in soils which contain exchangeable Ca, additions of any neutral salt would result in displacement of Ca into solution which, in turn, could lead to an increase in phosphate adsorption by

the hydrous oxides of soils as described above for gibbsite. Also, adding neutral salts to soil suspensions usually lowers the pH of the suspension (White, 1969), and this, in turn, increases phosphate adsorption by hydrous oxides (Muljadi et al., 1966a,b; Hingston, 1967).

In a second study on phosphate adsorption by gibbsite as affected by the formation of surface complexes involving divalent cations, Helyar et al. (1976b) suggested that divalent cations with a radius near 1.0 A° increase phosphate adsorption by this mineral. Thus, Ca, Cd, and Sr, which have been found to increase the adsorption and have crystal ionic radii of 0.99, 0.99, and 1.13 A°, respectively (Pauling, 1948), can fit the cavity between the phosphate ions pair without strains. The cations that do not affect phosphate adsorption, i.e., Mg, Zn, Na, and K, have ionic radii of 0.66, 0.74, 0.95, and 1.33 A°, respectively. Thus, the available space and charge of two adjacent adsorbed phosphate ions form a stable complex with a divalent cation if it is able to form coordinate bonds with two pairs of two resonant 0.5^- charge oxygen atoms in one plane and if it has a radius of about 1.0 A°. This explanation, however, is in contrast to the decrease in phosphate adsorption reported at low pH values in the presence of salts (Colwell, 1959).

Bowden et al. (1980a) proposed another reason (model) for phosphate adsorption by variable charge surfaces (goethite). They measured the effects of varying the concentration of NaCl and $CaCl_2$ on phosphate adsorption by goethite and tested the ability of their model to describe

these effects. They found that at low pH values, increasing the concentration of either salts decreased phosphate adsorption. But, with increasing pH, a point was reached at which there was no effect of salt concentration on adsorption; however, beyond that point, phosphate adsorption increased as salt concentration increased. According to the model proposed by Bowden et al. (1980a), the effect of the type of salt and its concentration affects the distribution of electrolyte near the surface: As a result, the electrostatic potential in the plane of adsorption will change. At low pH (positively charged surface), an increase in salt concentration decreases the potential in the plane of adsorption, thus decreasing the phosphate adsorption. At high pH (negatively charged surface), an increase in salt concentration makes the potential in the plane of adsorption less negative and, consequently, increases phosphate adsorption.

Posner and Bowden (1980) studied phosphate adsorption isotherms and calculated theoretical isotherms for a series of pH values and ionic strength by using the model proposed by Bowden et al. (1980a). They reported that at pH > zpc, increasing ionic strength depressed the electrostatic potential, thus reducing the repulsion between the surface and the specifically adsorbed phosphate ion. Consequently, the phosphate adsorption increased with increasing ionic strength. At pH < zpc, however, increasing the ionic strength again depressed the electrostatic potential, but phosphate adsorption decreased with increasing ionic strength.

A characteristic pH value above which increasing ionic strength increased adsorption of phosphate and below which the reverse occurred has also been reported for two surface soils of contrasting mineralogy and adjusted to several levels of pH values by HCl or $CaCO_3$ (Bolan et al., 1986). In general, increasing ionic strength increased the net surface charge by increasing the positive and negative charge below and above the zpc, respectively. If only coulombic forces were involved in ionic adsorption, increasing ionic strength should decrease adsorption of P at pH > zpc, and the reverse should be true for pH < zpc (Hingston, 1981). However, increasing ionic strength always increases phosphate adsorption above zpc and decreases phosphate adsorption below zpc (Ryden et al., 1977; Barrow et al., 1980b; Keren and O'Connor, 1982). This fact suggests that the effect of ionic strength on phosphate adsorption operates through its effect on electrostatic potential in the plane of adsorption rather than through its effect on surface charge.

In a study of the effect of ionic strength, pH, and time on phosphate adsorption by kaolinite and montmorillonite, Bar-Yosef et al. (1988) found that increasing electrolyte concentration decreased phosphate concentration in the solution phase in both clay systems. They suggested that this effect of ionic strength operates via their effect on the extent of the diffuse double layer, which determines the accessibility of phosphate ion to the adsorption sites on the clay edges.

Stoop (1983) studied phosphate adsorption by four Hawaiian soils and reported that after phosphate addition and equilibration in 0.01 M $CaCl_2$, $MgCl_2$, or KCl solution the phosphate concentration was much lower in solutions containing divalent cations than that in solutions containing monovalent cations. Barrow (1984) found that for six soils incubated with several levels of $CaCO_3$ or HCl, phosphate adsorption measured in 0.01 M $CaCl_2$ was higher than that measured in 0.01 M NaCl. Other studies by Singh and Tabatabai (1976) on the effect of 10 salt solutions on phosphate adsorption by six Iowa surface soils showed that when the equilibrating solution was made to contain 0.01 M with respect to $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, KCl, LiCl, NaCl, or $KHCO_3$, the amount of P adsorbed by soils always exceeded that adsorbed from a soil-water system. Their results also showed that, in addition to cations, the associated anions (and perhaps pH of the system) affected P adsorption by soils.

From the findings reported above, it is clear that the type and concentration of salts in the equilibration solution, and perhaps the cation-exchange capacity and exchangeable cations of soils, significantly affect phosphate adsorption by soils.

Effect of Exchangeable Cations on Phosphate Adsorption by Soils

Numerous investigators have reported that clays retained more phosphate when saturated with Ca than when saturated with H^+ (Allison, 1943; Chandler, 1941; Ragland and Seay, 1957; and Wild, 1953). Field

studies have generally shown that phosphate availability increases as Ca saturation of the exchange complex increases (Pierre, 1948). This was confirmed by Ellis and Truog (1955) who found that phosphate retention by montmorillonite, free of Fe and Al oxides, is due to formation of a calcium phosphate complex. A definite increase in phosphate retention with an increase in Ca saturation was reported for freshly acid-washed clay separates of five Kentucky soils (Calvert et al., 1960). However, aging the clays after acid-washing decreased phosphate retention as Ca saturation increased for the same clay separates. They attributed this to formation of calcium phosphates of greater solubility than aluminum phosphates or formation of basic aluminum phosphates, as previously suggested by Wild (1953). Considering the three cations that they studied, Calvert et al. (1960) also reported that phosphate retention by clays decreased in the order of the following exchangeable cations: H < Ca < Al.

Phosphate adsorption may be affected in numerous ways by mono or divalent cations added to a clay-phosphorus system. The cations may replace the Al ions, which in turn may precipitate with phosphate ions either in the equilibrium solution or in the diffuse double layer; thus the activity of the phosphate ions in both the equilibrium solution and the diffuse double layer is determined by the concentration and charge of the added cations (Wild, 1953). Aluminum on the clay surfaces, as hydroxy-Al polymers or as surface clay lattice Al, can adsorb P (Hsu,

1965). The thickness of the diffuse double layer is inversely proportional to the valencey of the saturating cation (Wiklander, 1964). The Donnan theory predicts that the activity of the phosphate ion in the vicinity of the clay particles should increase as the valency of the saturating cation increases. Thus, the accessibility of the clay surface to P in an adsorption reaction should be greater with divalent than with monovalent cations on the exchange complex.

The hypothesis that phosphate can be adsorbed by clay through the intermediary of exchangeable Ca ions have been proposed to account for adsorption of P by soils. This hypothesis was first put forward by Delmon and Barbier in 1930, as cited by Wild (1953), because they observed that a soil clay adsorbed less phosphate when acid saturated than when base saturated. Barbier and Chabannes (1949) found that acid clays titrated with $Ca(OH)_2$ adsorbed appreciably more phosphate than when titrated with KOH to the same pH value. Birch (1951) used this hypothesis to explain the high availability of phosphate in East African soils well supplied with Ca and concluded that the hypothesis is unlikely to be true unless a complex such as $(Ca(H_2PO_4))^+$ is formed. Wild (1953) considered the reasoning of the above theory improbable because he found that, for kaolinite, montmorillonite, and Rothamested clays saturated with different cations, the retention of phosphate in the presence of Cs or Ca ions was more than in the presence of Na ions. For the Rothamested clay at pH 5.5, the effect of exchangeable cations

was in the order: Li = Na < K < Rb < Cs < Ca < Sr < Ba. At low pH values, direct precipitation of phosphate by the metal added as alkali is improbable because the solubility products of the corresponding phosphate compounds are not exceeded. Also, with the monovalent ions, the bridging mechanism seems untenable and another theory, therefore, needed to be examined. Depending on the data that he obtained, Wild (1953) suggested that the cations influenced the extent to which Al and Fe, present in the clay, reacted with P.

Pissarides et al. (1968) investigated the influence of cation saturation on phosphate adsorption by three clay minerals (kaolinite, illite, and montmorillonite) saturated with different cations (Li, Na, K, Mg, Ca, Sr, and Ba) before equilibration with dilute P solutions. They found that the values of the phosphate adsorption maxima, as determined by the Langmuir model, were much higher for divalent than for monovalent cations, with the only exception in the case of K-illite. The abnormally high adsorption maximum obtained with K-illite was attributed to the interlayer adsorption of K which may cause a decrease of the negative charge on the clay and a corresponding increase of phosphate activity in the vicinity of the clay surface.

Curtin et al. (1987) evaluated the significance of exchangeable cations on the release of phosphate using sequential extraction with water for 11 acid (pH 5.5-6.3) New Zealand soils contrasting in P status and retention. They found that the release of P from Na-saturated soils exceeded that from the original Ca-dominated soils up to four-fold.

They explained this in terms of either enhancing the release of adsorbed phosphate following the removal of exchangeable Ca, increased dissolution of the calcium phosphate phase present as a surface complex, or as a metastable fertilizer reaction product.

Depending on the principles of surface charge balance outlined by Bowden et al. (1980a), the electrostatic potential of soil surfaces with a net negative charge will be more negative when the balancing cation is further from the surface. The more negative potential in the plane of adsorption, the less the amount of phosphate adsorption. Cation characteristics which determine the closeness of the cation from the surface are valence and the degree of the hydration. This may explain the finding of numerous investigators that replacement of Ca (and Mg) by more loosely bound Na ions would lead to less phosphate adsorption.

With samples of six soils from eastern Australia, Russell et al. (1988) found that P adsorption and buffering capacity increased with increasing $CaCl_2$-extractable Al and decreased with increasing exchangeable Na saturation or soil solution Na. Smillie et al. (1987) investigated the phosphate extractability from two weakly acid soils using an incubation study under field conditions. They found that a high portion (up to 80%) of the added P could be recovered by water extraction when exchangeable Ca was replaced by Na. Depending on this finding, they suggested that adsorbed phosphate may enter into chemical association with Ca, which may be an important mechanism of phosphate retention in

acid soils that contain adequate exchangeable Ca. Studies by Sharpley et al. (1988) showed that replacing indigenous exchangeable cations with Na, for 34 soils representing nine soil orders, stimulated the release of P; and Na-saturated soils released about 2.5 times more phosphate than the untreated soils. Their results also indicated that the distribution of P between solid-solution phases is strongly dependent on the nature of the exchangeable cations.

Effect of Organic Matter on Phosphate Adsorption by Soils

The effect of organic matter on phosphate adsorption and interaction with different soil constituents has been the subject of intensive investigations. The role of organic matter in phosphate adsorption is a dual one: either it can adsorb phosphate due to the positive charges which arise from metal cation-organic matter complexes (Williams, 1960) or organic matter can block potential phosphate sites on inorganic particles. The effect of organic anions such as citrate, malate, and oxalate on phosphate adsorption is of special interest because of the presence of polycarboxylic acids in soils, as a consequence of both root exudates and microbial activities in the rhizosphere zone (Louw and Webley, 1959; Mullette et al., 1974). Nagarajah et al. (1968) reported that phosphate adsorption by kaolinite in the presence of citrate or bicarbonate is reduced and the extent of the reduction depends on the order in which phosphate and citrate or bicarbonate are added to the

clay. Maximum reduction occurred when phosphate and citrate or bicarbonate are added together or when phosphate is introduced after citrate or bicarbonate adsorption.

The relative amount of inorganic phosphate associated with organic matter varies widely and represents not less than half of the total amount of P in the upper soil horizons (Williams et al., 1958). Soils with high concentrations of organic acids and soils with high organic matter contents have very high capacities to adsorb P (Fox and Kamprath, 1971). Sinha (1971) observed that labile undissociated organo-metallic phosphates were formed only when humic and fulvic acids complexed with Fe or Al.

The ability of different organic anions to compete for the adsorption site with phosphate has been suggested as a mechanism to explain the effect of organic anions on phosphate adsorption by soils (Deb and Datta, 1967a,b; Nagarajah et al., 1968, 1970). The effectiveness of organic anions in competing with phosphate for the available adsorption sites depends on the number and the type of their functional groups as well as the dissociation constants (Kwong et al., 1979a,b; Struthers and Sieling, 1950). Nagarajah et al. (1970) demonstrated that, of the most commonly occurring organic acids, anions of tricarboxylic acids were more effective in reducing phosphate adsorption than those of dicarboxylic acids. However, anions of monocarboxylic acids had little effect on phosphate adsorption. They also suggested that organic anions such as citrate, oxalate, poligalacturonate were specifically

adsorbed at M-OH (where M=Al or Fe) surfaces of soil components in a manner analogous to certain inorganic anions such as phosphate. The ability of organic anions to compete with phosphate for adsorption sites has been reported to be maximum at a pH equivalent to the pK_a values of the organic acids (Deb and Datta, 1967a,b). In contrast to that, Appelt et al. (1975) found that adsorption of simple organic anions that are specifically adsorbed blocked, to some extent, the adsorption sites for nonspecifically adsorbed anions such as Cl^- and/or NO_3^-. But organic anions did not compete for or block adsorption sites for phosphate in the volcanic ash-derived soils that they used. This controversy may be explained in terms of the excess adsorption sites available in the volcanic ash soils used by Appelt et al. (1975) to draw their conclusions. Concentration of organic anions is also considered to be an important factor determining their effectiveness in competition with phosphate. Earl et al. (1979) demonstrated that 10^{-3} M citrate was markedly effective in reducing phosphate adsorption (50% reduction), tartrate was only moderately effective (20% reduction), whereas acetate had little or no effect (1% reduction) at a final phosphate concentration of 0.2 mM for two contrasting soils and synthetic Fe and Al gels. At 10^{-2} M, citrate and tartrate removed 91% of Fe and 88% of Al from the Fe and Al gels, respectively, reducing the phosphate adsorption by 89 and 88%. They also found that the reduction in phosphate adsorption observed in the presence of citrate resulted from the elimination of a significant proportion of phosphate-sorbing sites, while the reduction

observed in the case of tartrate was through a combined dissolution-competitive adsorption effect.

The release of phosphate by organic anions from P-enriched acid and calcareous tropical soils has been shown to be affected by pH (3-12) in a rather specific form (Lopez-Hernandez et al., 1979). For both groups of soils, they attributed the effect of pH to either direct exchange between the dissociated organic anion and the phosphate ion, dissolution and chelation of active forms of Fe and Al, or partial hydrolysis of organic P compounds (at very low pH values).

Swenson et al. (1949) reported that several organic acids and organic-acid salts have the ability to prevent fixation of phosphate by Fe and Al. The results of the investigation by Marion and Thomas (1946) showed that organic acids which have the ability to form complexes with Fe and Al would be effective in replacing fixed phosphate. The effectiveness of organic anions in preventing the precipitation of phosphate by Fe and Al depends on the pH of the system. Struthers and Sieling (1950) found that, in the Fe system, tartrate prevented the precipitation of phosphate to a greater degree throughout the entire pH range of 3 to 8 than did other anions (alanin, aspartic, citric, malic, malonic, oxalic, succinic, and tartric acids) studied. The malate ion was effective below pH 6, and succinate and aspartic ions did not decrease the amount of phosphate precipitated by Fe at any pH value.

There is considerable evidence that humus is closely associated with the soil mineral fraction, especially with positively-charged colloidal particles such as sesquioxide, allophanes, and others present in the clay fraction of soils (Appelet et al., 1975; Satoh and Yamane, 1971). Sinha (1972) prepared stable organo-mineral phosphates of varying solubilities by direct interaction of humic acid and fulvic acid Fe complexes with phosphate. Weir and Soper (1963) found that the complex between Fe and the organic groups in humic acid extracts had the capacity to hold phosphate ions against an anion resin and the amount of phosphate held was a function of pH and type of resin used.

Schnitzer and Hansen (1970) found that between pH 3 and 5 at ionic strength (μ)=0.1 fulvic acid formed 1:1 molar (mononuclear) complexes with the following metal ions: Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Zn^{+}, Ca^{2+}, and Mg^{2+}. However, at the same μ value but at pH 1.7 and 2.35, fulvic acid also formed 1:1 complexes with Fe^{3+} and Al^{3+}, respectively. They also reported that the stability constant of these complexes increased with the increase in pH. The order of stabilities at low pH values was: Fe > Al > Cu > Ni > Co > Pb = Ca > Zn > Mn > Mg. Thus, the formation of stable complexes with cations responsible for phosphate retention will, in return, reduce phosphate fixation by soils.

MATERIALS AND METHODS

Soils

The soils used in this work (Table 1) were surface samples (0-15 cm) selected to give a wide range in chemical and physical properties. The field-moist soils were passed through a 6-mm screen, mixed thoroughly, placed in polyethylene bags, and stored in a refrigerator for later experiments. Another portion of each soil was allowed to air dry at room temperature, passed through a 2-mm sieve, and stored in closed glass containers. A subsample of the air-dried soil was ground to pass through a 100-mesh sieve (150 μm) for chemical analysis.

In the analyses reported in Table 1, the pH was determined by a combination glass electrode (soil:water ratio of 1:2.5), organic C by the method of Mebius (1960), total N by the semimicro-Kjeldahl procedure described by Bremner and Mulvaney (1982), inorganic N (NH_4^+ and NO_3^-) as described by Keeney and Nelson (1982). Organic and inorganic P were determined by the method of Olsen and Dean (1965), as modified by Chae and Tabatabai (1981). Exchangeable K was determined by the method of Pratt (1965), and exchangeable Ca and Mg by the method of Heald (1965). The cation exchange capacity was measured by the method of Chapman (1965). Dithionite-extractable Fe and Al were determined by the method of Jackson (1956) but using atomic absorption spectrophotometry for determination of Fe and Al. Particle-size distribution was determined by the pipette method of Kilmer and Alexander (1949).

The finely ground soil samples (<100 mesh) were used in determination of organic C, total N, organic P, inorganic P, and total P; while the <2 mm samples were used in the other analyses reported in Table 1.

All results reported are averages of duplicate determinations expressed on a moisture-free basis, moisture being determined by loss of weight after drying at 105°C for 48 h.

Table 1. Properties of the soils used

Soil No.	Soil Series	Soil Subgroup	pH[a] H_2O	pH[a] $CaCl_2$	Org. C
					g kg^{-1} soil
Iowa soils					
1	Hayden	Typic Hapludalf	5.8	5.1	8
2	Luther	Aeric Ochraqualf	6.4	5.6	13
3	Tama	Typic Argiudoll	5.4	5.1	22
4	Lester	Mollic Hapludalf	6.6	6.1	34
5	Clarion	Typic Hapludoll	6.2	5.4	34
6	Nicollet	Aquic Hapludoll	6.4	5.9	37
Costa Rica soils					
7	Hacienda Vieja	Typic Dystrandept	5.0	4.6	29
8	La Pinera	Ustoic Plehumult	4.6	4.1	37
Chilean soils					
9	Constitucion	Ultic Paleustalf	5.6	5.1	16
10	Osorno	Typic Dystrandept	5.3	4.9	84

[a]Soil:water or soil:0.01 M $CaCl_2$ ratio, 1:2.5.

Table 1. Continued

Soil no.	Nitrogen as			Phosphorus as		Sulfur as		Extractable[b]	
	Total	NH_4^+	NO_3^-	Org.	Inorg.	Org.	SO_4^{2-}	Fe	Al
	--g kg^{-1} soil--			---------- mg kg^{-1} soil ----------					
1	0.80	2	2	109	266	126	2.0	1350	561
2	1.02	6	7	160	171	122	3.2	1150	584
3	1.90	7	31	330	163	230	10.3	1635	1050
4	2.53	5	10	292	135	397	4.3	999	539
5	2.70	8	4	366	173	316	2.6	943	722
6	2.82	8	9	327	217	388	2.0	1250	811
7	3.00	15	46	1880	466	956	4.7	--	--
8	2.60	10	20	774	63	284	5.6	--	--
9	1.19	6	31	109	154	154	5.4	--	--
10	7.61	20	80	1196	767	892	1.9	--	--

[b]Sodium dithionite-extractable Al and Fe. (--) Indicates not determined.

Table 1. Continued

Soil no.	CEC	Exchangeable bases				Clay	Sand
		Na	K	Ca	Mg		
	---------cmol(+)/kg soil---------					--g kg^{-1} soil--	
1	10.5	0	0.4	6.1	1.4	140	530
2	14.0	0	0.3	8.9	1.1	170	330
3	18.6	0.1	0.5	9.2	1.9	230	50
4	19.5	0	0.5	15.0	2.6	160	330
5	25.9	0	1.0	10.0	3.9	230	310
6	25.8	0	1.5	16.2	2.1	210	400
7	34.8	0.1	0.9	8.0	1.7	380	280
8	25.6	0.1	0.1	0.4	1.8	660	120
9	9.3	0.1	0.1	5.9	2.1	140	640
10	52.4	0.1	1.5	9.7	1.7	310	170

PART I. DETERMINATION OF SURFACE CHARGE DENSITY OF SOILS

INTRODUCTION

Numerous methods have been proposed for determination of the surface charge density behavior of soils. These include cation-anion exchange, potentiometric titration, and electrokinetics methods (Schulthess and Sparks, 1986, 1988). The last method does not give information about the number of surface charge sites per unit area. To obtain such information, potentiometric titration data have been used. Potentiometric titration curves of soils, however, do not yield definite breaks to indicate the end point. Another problem is that the surface charge density predicted from potentiometric titration curves is extremely large at only a few pH units above and below the zero point of charge (zpc) (Schulthess and Sparks, 1988). Thus, the charge behavior of a soil or Al or Fe oxide sample is usually characterized by methods involving cation and anion exchange. This technique has become an acceptable method in soil research for determination of negative and positive charge densities. The potentiometric titration methods are generally reserved for zpc analysis only (Schulthess and Sparks, 1986).

Several cation-anion exchange methods have been proposed for determination of surface charge density since its introduction by Schofield (1949). Schofield's method involves equilibrating a 5-g sample with 0.2 M NH_4Cl to saturate the negative and positive exchange sites with NH_4^+ and Cl^-, respectively. The exchanged ions are removed

by extraction with 0.2 M KNO_3, and the amounts of NH_4^+ and Cl^- released are determined. The net amounts of NH_4^+ and Cl^- exchanged are calculated by subtracting the amounts of these ions present in the sample solution after centrifuging; assuming that the ratio of water to chloride is the same as the original NH_4Cl solution. Since Schofield published his work, several modifications of this method have been used, but without thorough evaluation (Marsh et al., 1987; Van Raij and Peech, 1972; Hingston et al., 1974; Wada and Okamura, 1980). These modifications involved replacing the NH_4Cl saturating solution with NaCl solutions ranging in concentrations from 0.01 to 1 M, various soil or clay:solution ratios, and replacing the extracting solution with NH_4NO_3 ranging in concentrations from 0.1 to 0.5 M. All these methods involve several steps of equilibrations, washings, and extractions. In this work, we investigated the use of 1 M NH_4NO_3 as a saturating solution and determination of the NH_4^+ and NO_3^- retained by steam distillation in the presence of 2 M NaCl to estimate both negative and positive charge densities. The results obtained by this method were compared with those obtained by the Schofield method (1949) and by four modified Schofield methods (Marsh et al., 1987; Van Raij and Peech, 1972; Hingston et al., 1974; Wada and Okamura, 1980).

DESCRIPTION OF METHODS

Soils

The soils used (Table 2) were surface samples selected to represent cultivated soils of Iowa, Chile, and Costa Rica and to obtain a wide range of pH, texture, and organic C content. Before use, the soils were passed through a 2-mm mesh sieve. A subsample of each soil was air-dried and ground to pass a 100-mesh sieve (150 μm) for determination of organic C, surface area, and surface charge density. The other analyses were performed on the coarser (<2-mm) soil samples. These and the other properties reported in Table 1 were determined as described in the Materials and Methods section. The surface area (Table 3) was determined by the method of Heilman et al. (1965).

In the other five methods evaluated (Table 4), NH_4^+ was determined by steam distillation (Keeney and Nelson, 1982), Na^+ by atomic absorption spectrophotometry, and Cl^- by the mercuric thiocyanate and ferric ammonium sulfate method of Iwasaki et al. (1952).

Reagents

Ammonium nitrate (1 M): 80 g of NH_4NO_3 was dissolved in about 700 mL of deionized water, and the volume was adjusted to 1 L with water.

Ammonium nitrate (0.1 M): 100 mL of 1 M NH_4NO_3 was diluted to 1 L with water.

Table 2. Properties of soils used

Soil	pH[a]		Org. C	CEC[b]	Clay	Sand
	H_2O	$CaCl_2$				
			-%-		-----%-----	
Hayden	5.8	5.1	0.8	10.5	14	53
La Pinera[c]	4.6	4.1	1.2	23.6	67	13
Luther	6.4	5.6	1.3	14.0	17	33
Constitucion[d]	5.6	5.1	1.6	15.1	18	40
Tama	5.4	5.1	2.2	18.6	23	5
Clarion	6.2	5.4	3.4	25.9	23	31
Lester	6.6	6.1	3.4	19.5	16	23
Hacienda Vieja[c]	5.0	4.5	3.7	34.8	38	28
Nicollet	6.4	5.9	3.7	25.8	20	40
Osorno[d]	5.3	4.6	8.4	52.4	31	17

[a]Soil:water or soil:0.01 M $CaCl_2$ ratio, 1:2.5.

[b]Cation-exchange capacity [cmol (NH_4^+) kg^{-1} soil].

[c]Soils from Costa Rica.

[d]Soils from Chile.

Table 3. Surface area of the soils used

Soil	Surface area	
	<2 mm	<150 μm
	$m^2 g^{-1}$	
Hayden	34.5	37.3
La Pinera	59.2	78.9
Luther	34.9	39.1
Constitucion	14.8	16.4
Tama	46.8	51.8
Clarion	48.3	66.4
Lester	49.1	60.2
Hacienda Vieja	77.1	96.6
Nicollet	66.1	73.4
Osorno	114.9	135.6
Avg.	54.6	65.6

Table 4. Conditions of the methods studied

Method[b]	Weight of soil	Saturating solution		Extracting solution[a]	
		Salt	Volume	Salt	Volume
	g		mL		mL
A	5	0.2 M NH_4Cl[c]	50	0.2 M KNO_3	50(5)
B	3	0.1 M NaCl	30	0.1 M KNO_3	10(5)
C	2	1.0 M NaCl	50	0.5 M NH_4NO_3	20(5)
D	1	0.01 M NaCl	25	0.1 M NH_4NO_3	25(3)
E	0.5	1 M NH_4Cl	30	1 M $NaNO_3$	10(5)
F	1	1 M NH_4NO_3	20	None	None

[a]Figures in parentheses refer to number of extractions.

[b]Methods: A, Schofield (1949); B, Marsh et al. (1987); C, Van Raij and Peech (1972); D, Hingston et al. (1974); E, Wada and Okamura (1980); F, proposed. With the exception of method E, which involved using 150-μm particle-size soil samples, all other methods involved using <2-mm samples.

[c]0.2 M NH_4Cl made in 1 mM HCl (final pH = 3.05). The pH values of the other saturating solutions listed were: 5.90, 6.45, 5.50, 4.78, and 4.82, respectively.

Sodium chloride 2 M: 117 g of NaCl was dissolved in about 700 mL of deionized water, and the volume was adjusted to 1 l with water.

Reagents for steam distillation of NH_4^+ and NO_3^-: Prepared as described by Keeney and Nelson (1982).

Procedures

A sample of soil (1.000 g, <2-mm) in a 50-mL preweighed polypropylene centrifuge tube was treated with 20 mL of 1 M NH_4NO_3 and

equilibrated for 24 h at 25°C (the tube was stoppered and shaken horizontally on an end-to-end shaker). The suspension was then centrifuged at 27,160 x g, the supernatant was discarded, and the residue was washed three times with 20 mL of 0.1 M NH_4NO_3 (by mixing and centrifuging). The centrifuge tube and its content were weighed again, and the entrained NH_4NO_3 solution was calculated. The soil in the centrifuge tube was quantitatively transferred into a 250-mL distillation flask by using 20 mL of 2 M NaCl. The NH_4^+ and NO_3^- contents of the sample were then described by Keeney and Nelson (1982). The amounts of NH_4^+ and NO_3^- retained by the soil sample were calculated by subtracting the amounts of these ions in the entrained solution from the values obtained by the steam distillation method, assuming that the concentrations of the ions in the entrained solution were the same as those of the 0.1 M NH_4NO_3 washing solution.

Unless otherwise indicated, all results reported are averages of duplicate determinations expressed on a moisture-free basis, moisture being determined from weight loss after drying at 105°C for 48 h.

RESULTS AND DISCUSSION

The surface areas of the soils ranged from 14 to 114.9 $m^2\ g^{-1}$ soil (avg. = 54.6 $m^2\ g^{-1}$ soil) for the <2-mm samples and from 16.4 to 135.6 $m^2\ g^{-1}$ soil (avg. = 65.6 $m^2\ g^{-1}$ soil) for the <150-μm soil samples. As expected, grinding the soil samples resulted in increases in surface areas (Table 3). These results should allow, if desired, to calculate the surface charge densities in terms of charge per unit area.

Table 4 shows the conditions of the methods studied. Although the original Schofield method (1949) involved saturation of clay exchange sites with NH_4^+ and Cl^- by using NH_4Cl and extraction of these ions with KNO_3, the modification of this method by Marsh et al. (1987), Van Raij and Peech (1972), and Hingston et al. (1974) involved saturation with Na^+ and Cl^- by using 0.1 M, 1.0 M, and 0.01 M NaCl, respectively, and extraction of the retained cations and anions with 0.1 M KNO_3, 0.5 M NH_4NO_3, and 0.1 M NH_4NO_3. The ratio of the volume of the saturating solution to clay or to soil ranged from 10:1 to 25:1. Wada and Okamura (1980) used 1 M NH_4Cl as a source of saturating ions with a solution-to-soil ratio of 60:1 and determined these ions after extraction with 1 M $NaNO_3$. Neither of these four modifications have previously been evaluated to compare their results with those obtained by the original Schofield (1949) method or to report on their precision.

The results reported in Table 5 show that the surface negative charge densities of the 10 soils studied, expressed in cmol (-) kg^{-1}

Table 5. Comparison of surface negative charge density obtained by present methods and the proposed method

Soil	Surface negative charge density by method specified[a]						LSD
	A	B	C	D	E	F	($P<0.05$)
	cmol (-) kg^{-1}						
Hayden	9.1	7.3	10.1	1.5	15.0	10.0	0.95
La Pinera	9.9	2.5	4.6	0.85	16.7	7.0	0.30
Luther	11.6	8.8	11.9	1.6	19.7	13.2	1.87
Constitucion	8.7	9.9	10.2	1.6	13.9	10.1	1.59
Tama	13.7	6.7	15.0	1.7	20.0	15.4	1.10
Clarion	20.6	12.0	18.8	2.2	28.6	21.2	1.30
Lester	15.9	10.2	14.7	1.7	16.1	17.2	1.34
Hacienda Vieja	13.7	8.9	12.7	1.7	20.5	12.9	1.67
Nicollet	19.2	13.4	21.0	2.2	27.6	21.2	2.51
Osorno	14.9	9.4	15.1	2.5	23.5	18.0	1.99
Avg.	13.7	16.9	13.4	1.8	20.2	14.6	

[a]For method designation, see footnote of Table 4.

soil, were the greatest by the method of Wada and Okamura (1980) and the least by the method of Hingston et al. (1974), followed by the results obtained by the method of Van Raij and Peech (1972) and by the method of Marsh et al. (1987). Most of the results obtained by the proposed method agreed with those obtained by the original Schofield method. The significant difference among the surface negative charge densities reported in Tables 5 and 6 are expected considering the type

Table 6. Comparison of surface negative charge density of soils (expressed on a surface-area basis) obtained by present methods and the proposed method

Soil	Surface negative charge density by method specified[a]						LSD
	A	B	C	D	E	F	($P<0.05$)
	----------μmol(-) m^{-2}----------						
Hayden	2.62	2.13	2.94	0.42	4.02	2.89	0.272
La Pinera	1.24	0.425	0.78	0.145	2.11	1.06	0.051
Luther	3.33	2.53	3.41	0.458	5.04	3.78	0.536
Constitucion	5.90	6.68	6.91	1.08	8.46	6.81	1.05
Tama	2.92	1.44	3.21	0.370	3.86	3.28	0.218
Clarion	4.27	2.48	3.89	0.455	4.31	4.39	0.269
Lester	3.23	2.08	2.99	0.352	2.67	3.50	0.271
Hacienda Vieja	1.78	1.15	1.65	0.220	2.12	1.67	0.217
Nicollet	2.91	2.03	3.18	0.326	3.76	3.20	0.376
Osorno	1.29	0.821	1.13	0.218	1.74	1.57	0.167

[a]For method designation, see footnote of Table 4.

and concentration of ions of the four ion-saturating solutions employed and soil-to-solution ratios used. Other factors that affect the negative charge densities of soils are the type and concentration of the extractants and number of extractions used to release the retained positively and negatively charged ions. Because the surface negative charge densities were determined at or near soil pH values, for most soils, especially the highly acid soils from Costa Rica and Chile, these values were lower than those obtained for the CEC values determined at pH 7.0.

The difference between the CEC Values (Table 2) and those obtained by the Schofield method (1949) or the proposed method are due to the pH-dependent charges formed by raising the soil pH to 7.0 for CEC determination, especially for the acid soils.

The positive charge density values were much lower than those of the negative charge densities (Tables 5-8). The results obtained for surface positive charge densities of the 10 soils (Table 7), expressed in cmol (+) kg^{-1} soil, were the greatest by the method of Wada and Okamura (1980) and the least by the method of Hingston et al. (1974), followed by the values obtained by the method of Van Raij and Peech (1972). The negative charge density values obtained by the proposed method were lower than those obtained by the original Schofield method (1949). The variable type and concentration of ion-saturating solutions and the type of the extracting solutions used explain the observed difference in the negative charge density values obtained by the different methods studied (Tables 7 and 8). The acid soils from Costa Rica and Chile contained the greatest surface positive charge densities, especially by the method of Schofield (1949). This is expected because of the positively charged Al and Fe hydrous oxides present at low pH values, especially in volcanic ash soils such as those used from Costa Rica and Chile.

The precision of the proposed method is illustrated by Table 9, which gives the results of replicated analyses of four soils. Each soil was replicated eight times. The surface negative charge densities by

Table 7. Comparison of surface positive charge density of soils obtained by present methods and the proposed method

Soil	Surface positive charge density by method specified[a]						LSD ($P<0.05$)
	A	B	C	D	E	F	
	cmol (+) kg^{-1}						
Hayden	3.2	1.8	2.8	0.84	4.8	0.92	0.52
La Pinera	9.0	1.9	3.5	1.0	10.4	3.5	1.01
Luther	3.4	1.5	2.7	0.73	6.2	1.4	0.98
Constitucion	5.0	3.2	2.5	0.87	5.0	1.0	0.70
Tama	2.9	1.3	2.1	0.83	5.0	1.3	0.60
Clarion	1.5	1.1	2.5	0.90	6.6	0.30	0.93
Lester	2.9	1.4	2.1	0.78	5.5	1.9	1.05
Hacienda Vieja	8.5	1.4	1.8	0.70	7.2	1.4	0.96
Nicollet	2.6	1.5	3.9	0.85	5.0	1.8	0.96
Osorno	6.6	2.0	2.9	0.84	6.6	4.0	1.71
Avg.	4.6	1.7	2.7	0.30	6.2	1.8	

[a]For method designation, see footnote of Table 4.

Table 8. Comparison of surface positive charge density of soils (expressed on a surface-area basis) obtained by present methods and the proposed method

Soil	Surface positive charge density by method specified[a]						LSD ($P<0.05$)
	A	B	C	D	E	F	
	----------μmol (+) m^{-2}----------						
Hayden	0.920	0.525	0.805	0.240	1.280	0.270	0.141
La Pinera	1.52	0.320	0.591	0.169	1.32	0.591	0.171
Luther	0.974	0.430	0.774	0.209	1.59	0.401	0.281
Constitucion	3.38	2.16	1.69	0.588	3.05	0.676	0.473
Tama	0.610	0.270	0.441	0.178	0.960	0.280	0.125
Clarion	0.308	0.224	0.514	0.177	0.996	0.064	0.191
Lester	0.588	0.285	0.426	0.159	0.918	0.378	0.212
Hacienda Vieja	1.10	0.182	0.233	0.091	0.745	0.182	0.125
Nicollet	0.399	0.224	0.590	0.128	0.681	0.274	0.143
Osorno	0.574	0.174	0.252	0.073	0.487	0.348	0.149

[a]For method designation, see footnote of Table 4.

Table 9. Precision of the proposed method

Soil	Surface charge density[a] Range	Mean	SD	CV[b]
	-----cmol (-) kg^{-1} soil------			%
Hayden	9.30-10.2	9.8	0.34	3.4
Hacienda Vieja	12.5-14.1	13.4	0.59	4.0
Nicollet	19.9-21.7	21.0	0.68	3.3
Osorno	17.0-18.9	17.9	0.63	3.5
	-----cmol (+) kg^{-1} soil------			
Hayden	0.8-1.3	1.0	0.16	16.6
Hacienda Vieja	1.4-2.0	1.7	0.22	13.2
Nicollet	1.4-1.8	1.5	0.15	10.1
Osorno	3.2-4.8	4.0	0.58	14.5

[a]Range of eight replications; SD, standard deviation.
[b]CV, coefficient of variation.

the method described are highly reproducible, with coefficients of variation generally below 4%. Because of the low surface positive charge densities of the four soils tested, the coefficients of variation were much higher (<17%) than those of the negative charge densities (Table 9).

PART II. EFFECT OF pH ON PHOSPHATE ADSORPTION BY SOILS

INTRODUCTION

The pH is probably the most important operating factor affecting the adsorption of P by soils. This is because changes in pH may affect the phosphate adsorption through its effect on: (1) the phosphate ion species most abundant at that particular pH (Lindsay, 1979), which in turn affects the phosphate adsorption by soils (Bowden et al., 1980b; Taylor and Ellis, 1978; Parfitt et al., 1975); (2) pH also affects the electrostatic potential of the plane of adsorption and, therefore, the net positive charges (Bowden et al., 1980a; Kwong et al., 1979a; Van Raij and Peech, 1972; Bell and Gillman, 1978); (3) through its effect on the rate of mineralization of soil organic P (Haynes, 1982); (4) through the precipitation of exchangeable Al as a polymeric compound at high pH values (McLean, 1976; Sims and Ellis, 1983); and (5) through its effect on the amount of P released from soils because soils are usually at different initial P status (Barrow, 1984).

It was reported by Deb and Datta (1967a,b), Parfitt (1978), Bolan et al. (1986), and Cabrera et al. (1981) that the phosphate adsorption by soil increases as the pH decreases and the highest amount of phosphate adsorption is observed at low pH values (pH 3-4). In contrast to those reports, Murrmann and Peech (1969) found that for any given soil the amount of labile phosphate and phosphate concentration in soil solution were minimum values at about pH 5.5 and increased rapidly as the pH was increased or decreased from this value by the addition of $Ca(OH_2)$

or HCl, respectively. Moreover, there are conflicting reports about the effect of increasing the pH by liming on phosphate adsorption by soils. The most recent reviews by Sanchez and Uehara (1980), Probert (1980), and Haynes (1982) on this topic have concluded that liming increases, decreases, or does not affect the phosphate adsorption by soils.

Studies of phosphate adsorption isotherms of soils adjusted to different pH values by means other than liming are scarce. Adsorption isotherms, however, have been constructed for clay minerals adjusted to different pH values by using buffered solutions adjusted to different pH values (Hsu and Rennie, 1962) or by using a large liquid/clay ratio to maintain constant pH without a buffer (Muljadi et al., 1966a). In the case of using buffered solutions, the effect of pH on phosphate adsorption might be affected by the ions of the buffer used in competing with phosphate for the adsorbing sites. Other studies with soils have been limited to a single point adsorption measurement (Misra and Ojha, 1970; Chu and Sherman, 1952; Obihara and Russell, 1972) rather than multipoint isotherms.

Thus, the objective of this part was to study the effect of pH on phosphate adsorption by soils adjusted to a wide range of pH values without introducing buffer, phosphate-reactive ions and without using a large solution/soil ratio. Multipoint adsorption isotherms rather than a single measurement were used to evaluate the effect of pH.

DESCRIPTION OF METHODS

Soils

The soils used in this study were Hayden, Luther, Tama, Lester, Clarion, and Nicollet soils. These soils were chosen because of their similarity in pH values and because they gave a range in organic matter content and cation-exchange capacity. The pertinent properties of these soils are reported in Table 1, Materials and Methods section.

Adjustment of soil pH

The amounts of H^+ and OH^- required to adjust the soil pH from pH 3 to 8 were determined by titrating the soils with 0.01 M HCl or 0.01 M KOH. The titration process was carried out by placing 1 g of soil in a 50-mL beaker containing 25 mL of 0.01 M KCl by using a combination pH electrode. The soil particles were kept in suspension by a magnetic stirring bar and magnetic stirrer. All the titrations were done in duplicates.

Determination of zero point of charge

The electrical charges on the surfaces of soils were determined by acid-base potentiometric titration procedure similar to that described by Laverdiere and Weaver (1977). In brief, this procedure involves titration of a 5-g (<2 mm) soil sample in 50 mL of 0.01 M, 0.1 M, or 1 M NaCl with a standard 0.1 M HCl or 0.1 M NaOH in the presence of a pH electrode. Continuous stirring was maintained by using

a Teflon stirring bar and magnetic stirrer. Blank titrations were carried out on the same volume of the NaCl solutions and the amount of H^+ or OH^- required to adjust the soil at a given pH was calculated; the amount of H^+ or OH^- adsorbed by a soil at a given pH was taken as the amount added minus the amount of H^+ or OH^- required to bring a blank solution of the same volume and salt concentration to the same pH.

Preparation of NH_4-saturated soils

The soils were converted to a monoionic (NH_4^+) form by equilibrating 50 g of soil with 500 mL of neutral, 1 M NH_4OAc in a 1-liter Erlenmeyer flask. The flask was stoppered and shaken at 25°C on an end-to-end shaker for 24 h. After the equilibration, the flask was unstoppered, and the soil suspension was filtered by using a 12-cm Buchner funnel and Whatman No. 42 filter paper under light suction. The soil was leached with neutral, 1 M NH_4OAc until Ca could not be detected, then leached once with 1 M NH_4Cl and once with 0.25 M NH_4Cl. The electrolyte was washed out by 150-200 mL of isopropyl alcohol. When the test for Cl in the leachate (by using 0.1 M $AgNO_3$) became negligible, the soils were allowed to drain thoroughly, air-dried, then passed through a 2-mm sieve and stored in a closed glass container.

Reagents

Stock solutions

Potassium phosphate solution (3.23 mM, 100 μg P mL^{-1}): One liter of this solution was prepared by dissolving 0.4394 g of KH_2PO_4 in a

1-liter volumetric flask containing about 500 mL deionized water, and the volume was made up with deionized water.

Potassium chloride solution (0.1 M): One liter of this solution was prepared by dissolving 7.456 g of KCl in a 1-liter volumetric flask containing about 500 mL deionized water, and the volume was made up with deionized water.

Phosphate working solutions

Ten standard working solutions (0, 0.032, 0.161, 0.323, 0.484, 0.646, 0.807, 0.969, 1.13, and 1.29 mM; i.e., 0, 1, 5, 10, 15, 20, 25, 30, 35, and 40 μg P mL^{-1}) were prepared by adding 0, 1, 5, 10, 15, 20, 25, 30, 35, or 40 mL of the phosphate stock solution to a 100-mL volumetric flask containing 10 mL of 0.1 M KCl and enough H^+ or OH^- to be sufficient to adjust the soil pH to 4, 6, or 8 (the amount of HCl or NaOH required was previously determined by titration). The volume was adjusted so that the solution was 0.01 M with respect to KCl.

A separate set of the standard working solutions containing the required amount of H^+ or OH^- to maintain the soil and the equilibration solution at a desired pH value was prepared for each of the soils used.

Determination of the phosphate adsorption isotherms

Phosphate adsorption values were obtained by equilibrating 1 g of soil sample in a 50-mL plastic centrifuge tube with 25 mL of one of the phosphate working solutions. Three drops of chloroform were added to inhibit the microbial activity, the tube was then stoppered and

placed in a temperature-controlled (25°C) reciprocating shaker. The sample was shaken for 24 h at a shaking speed rate enough to keep the soil particles in suspension. After the equilibration time, the tube was unstoppered, pH was determined, and centrifuged at 12000 x g for 7 min. The supernatant was filtered through a 0.45-μm membrane (MSI Micron Separations, Inc.), and the filtrate was reserved for P analysis.

The phosphate remaining in the clear filtrate was determined colorimetrically by the method of Murphy and Riley (1962) as modified by Watanabe and Olsen (1965). All analyses reported were an average of duplicate determinations. The amount of phosphate adsorbed was calculated by subtracting the amount of P remaining in the equilibrium solution from that initially added. The Langmuir equation was used to calculate the adsorption maxima and the adsorption affinity coefficients.

Effect of pH on phosphate adsorption by soils

Phosphate adsorption as a function of pH was obtained for natural and NH_4-saturated soils at pH values ranging from 3 to 8 at 0.5 pH intervals. One-gram soil sample and 25 mL of 0.01 M KCl containing 1000 μg P (32.29 μmol P) and the amount of either H^+ or OH^- required to adjust the soil to the pH desired were added to a 50-mL plastic centrifuge tube. The microbial activity was inhibited by adding three drops of chloroform, and the tube was stoppered and shaken at 25°C for 24 h on a reciprocating shaker. After the equilibration time, the tube

was unstoppered, pH was measured, and centrifuged at 12000 x g for 7 min. The filtrate thus obtained was passed through a 0.45-μm membrane filter and the P remaining in the equilibrium solution was determined as described previously. The amount of P adsorbed by the soil sample was calculated by subtracting the amount of P remaining in the equilibrium solution from that initially added.

Effect of pH on desorption and release of phosphate

In one experiment, 1 g of soil sample was equilibrated, in a pre-weighed 50-mL plastic centrifuge tube, with 25 mL of 0.01 M KCl containing 1000 μg P (32.3 μmol P); and the amount of H^+ or OH^- as HCl or NaOH, respectively, required to adjust the soil to the pH desired were added. The soil-phosphate solution was equilibrated at 25°C for 24 h, and the amount of P adsorbed by soil was calculated as described before. The desorption of the adsorbed P was studied as will be described below.

In a second experiment, 1 g of soil sample was equilibrated with 25 mL of 0.01 M KCl containing the required amount of H^+ or OH^-, but without P. The soil-0.01 M KCl was equilibrated at 25°C for 24 h, and the amount of P released was determined by analyzing for P as described before.

In both experiments, the microbial activity was inhibited by adding three drops of chloroform. After the equilibration time, the tube was unstoppered, the pH was determined, and then centrifuged at 27160 x g

for 10 min. The clear supernatant was transferred into a 50-mL glass bottle and reserved for further P analysis as described before. The tube was weighed again to calculate the entrained solution.

Five to eight consecutive equilibrations were done on the soil sample in both experiments to desorb the added P or to release the native P. This was accomplished by weighing the tube after centrifuging and decanting the supernatant to calculate the entrained solution, and adding 25 mL of fresh 0.01 M KCl without P and repeating the P extraction as described above for five to eight times until release of the adsorbed or native P was negligible.

All equilibrations were done for 24 h because work by Nair et al. (1984) and Busman (1984) showed that this time is sufficient to establish equilibrium in P concentrations between the soil and solution phases.

RESULTS AND DISCUSSION

Isotherms showing the relation between the amount of phosphate adsorbed and the phosphate concentration in equilibrium solution at pH values of 4, 6, and 8 are presented in Figure 1 for Hayden, Luther, and Lester soils; and the corresponding results for Tama, Clarion, and Nicollet soils are shown in Figure 2. These curves show that phosphate adsorption by all soils was the least at pH 4 and the greatest at pH 8, as indicated by the relative location of the adsorption isotherms. These curves also show that, at the same equilibrium P concentration, different soils adsorbed different amounts of phosphate. In addition to the soil pH, other soil properties affect P adsorption by soils. These include clay content, exchangeable Al and Fe and their hydrous oxides, ionic composition of soils (both on the exchange sites and in solution), and organic matter content. As shown in Figures 1 and 2, the relationship between the amount of P adsorbed and its concentration in the equilibrium solution was curvilinear. Giles et al. (1960) attributed this nonlinear increase in phosphate adsorption to the progressive decrease in the sites available for the solute (phosphate ions) adsorption. Thus, the curvature shows that more adsorbing sites are filled and the system is close to saturation. Although P adsorption isotherms for all the soils at different pH values showed a distinct initial curvature, no real saturation zone is found. This could be attributed to the slow reaction that followed the initial rapid phosphate adsorption reaction (Barrow and Shaw, 1975).

Figure 1. Effect of pH of soil-0.01 M KCl equilibration system on the relationship between the amounts of phosphate-P adsorbed (X) and phosphate concentration in the equilibrium solution (C) for Hayden, Luther, and Lester soils

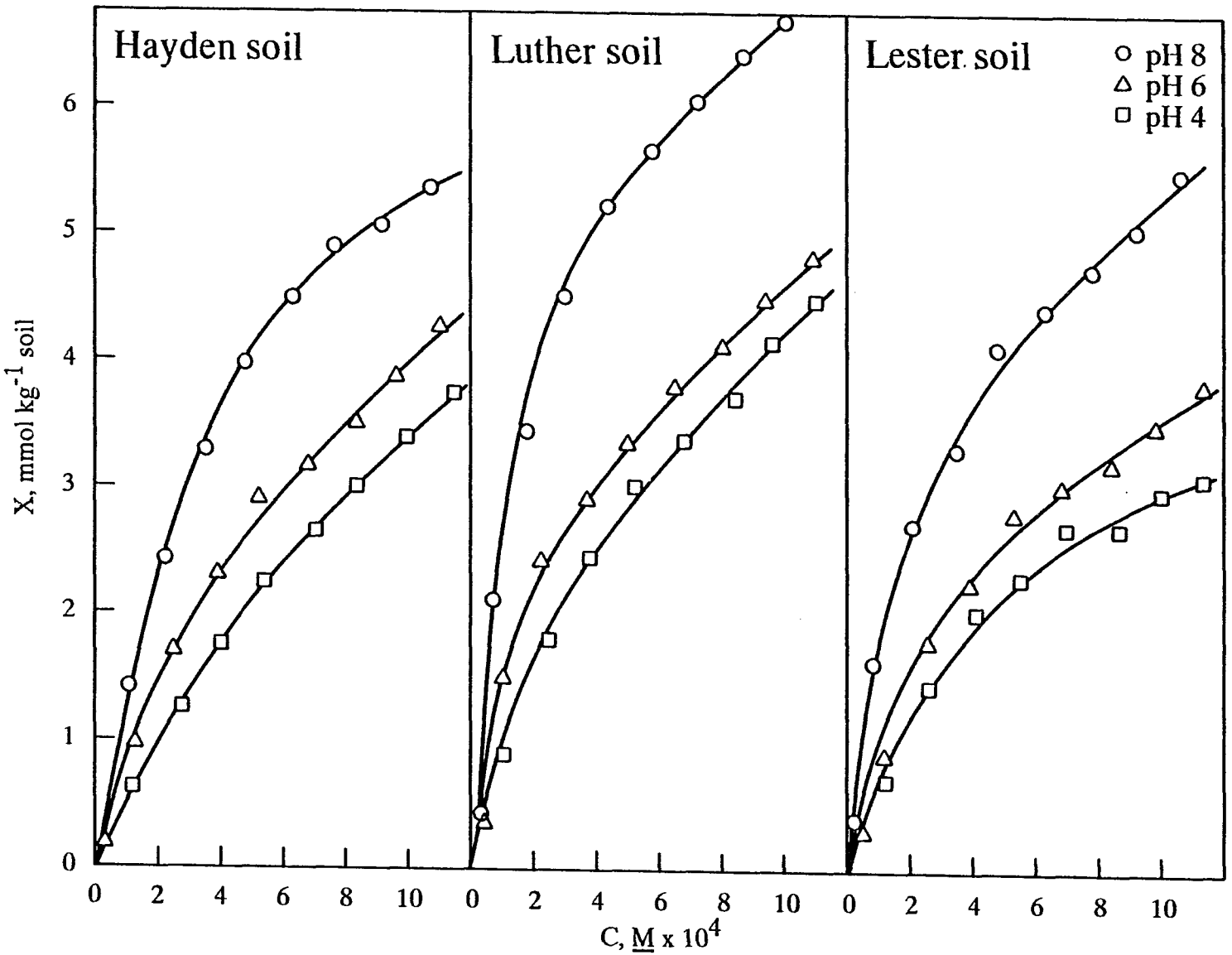
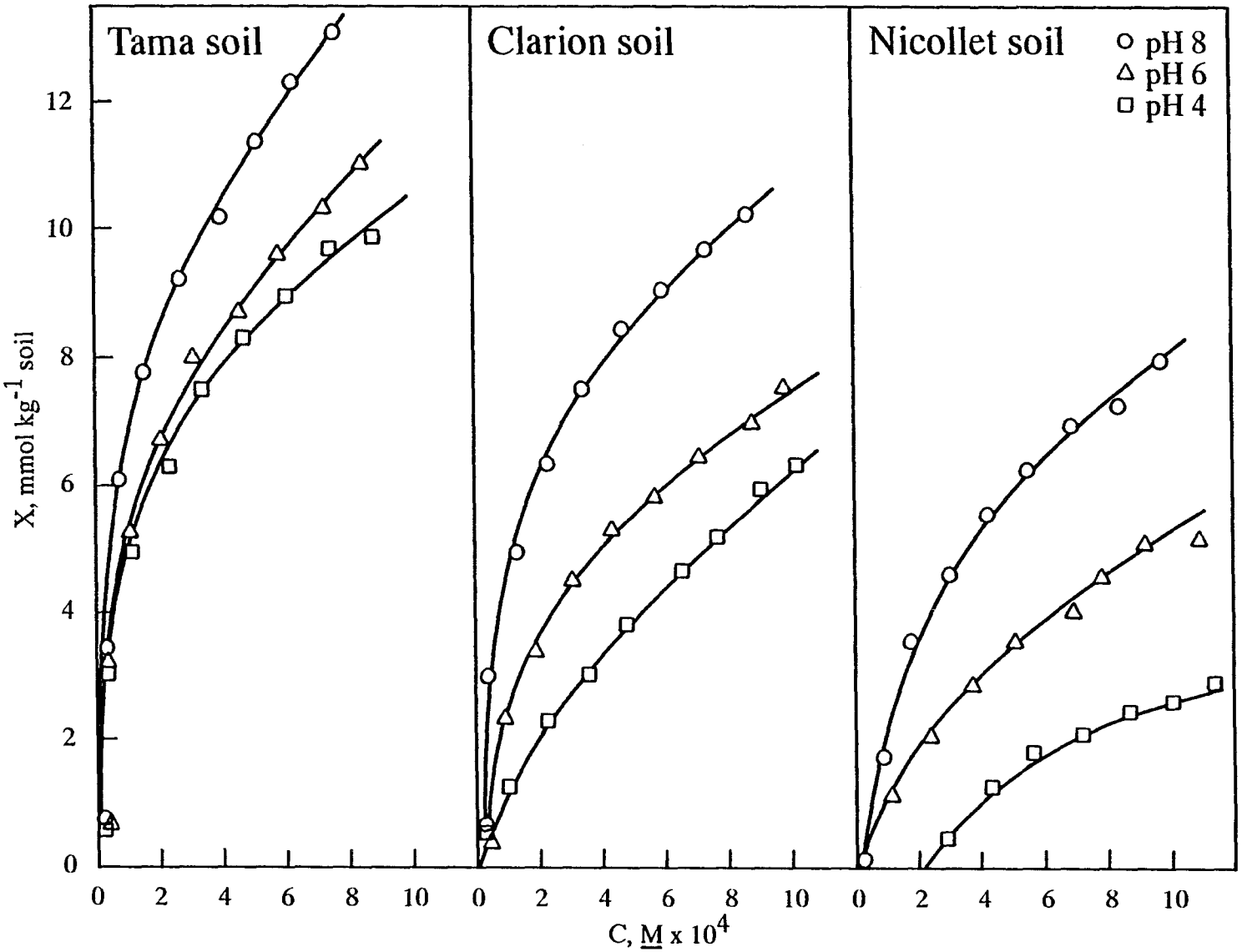

Hayden soil
Luther soil
Lester soil
pH 8
pH 6
pH 4
X, mmol kg-1 soil
C, M x 10^4
0
1
2
3
4
5
6
0
2
4
6
8
10

Figure 2. Effect of pH of soil-0.01 M KCl equilibration system on the relationship between the amounts of phosphate-P adsorbed (X) and phosphate concentration in the equilibrium solution (C) for Tama, Clarion, and Nicollet soils


Tama soil
Clarion soil
Nicollet soil
pH 8
pH 6
pH 4
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12

It is well known that the many results of adsorption isotherms can be summarized by a few numbers, and the adsorption process can be better understood by equations that describe the adsorption of P by soils. In fact, several equations have been used to describe the P adsorption by soils, with most workers favoring the Langmuir model, which is described by the following equation:

$$X = \frac{kCX_m}{1 + kC} \quad . \qquad [1]$$

Where X is the amount of phosphate adsorbed; C is the concentration of P in the equilibrium solution; X_m is the adsorption maximum; and k is an affinity coefficient. The equation can also be written in the following linear form:

$$\frac{C}{X} = \frac{1}{kX_m} + \frac{1}{X_m} C \quad . \qquad [2]$$

A plot of C/X against C should give a straight line of slope = $1/X_m$, from which X_m can be calculated; and the constant, k, is calculated from the intercept, $1/kX_m$. The Langmuir equation has been recommended over the other equations (e.g., Freundlich equation) because an adsorption affinity coefficient and an adsorption maximum can be calculated (Olsen and Watanabe, 1957). The other reason for not using the Freundlich equation is that it is an empirical equation and the constants have no meaning (Holford et al., 1974; Olsen and Watanabe, 1957).

The Langmuir adsorption isotherms resulting from the data of the P adsorption of Hayden and Clarion soils at pH values of 4, 6, and 8

are shown in Figure 3. Similar plots were obtained for adsorption of P by the other four soils examined. The resulting values of k, the affinity coefficient, and X_m, the adsorption maximum, for the adsorption of P by the soils examined are presented in Table 10. The adsorption maxima for Tama, Lester, and Nicollet soils were the greatest at pH 8 and the least at pH 6. This value for the Clarion soil at pH 6 was equal to that at pH 8. However, for the other two soils, Hayden and Luther soils, the adsorption maxima were the greatest at pH 4 and decreased to the lowest value when the pH increased to 6 to 8.

The order of adsorption maxima obtained from the Langmuir model at different pH values differed from the order of the location of the P adsorption isotherms in Figures 1 and 2. This discrepancy may be due to the slow adsorption reaction rates which followed the initial rapid adsorption reactions (Barrow and Shaw, 1975). The affinity coefficient values, k constant, showed least affinity for phosphate adsorption at the lowest pH (pH 4) and increased as the pH increased, being the greatest at pH 8 (Table 10). The relatively high affinity coefficients obtained for Tama, Clarion, and Luther soils could be attributed to the high level of extractable Al (Table 1). However, this was not the case for Nicollet soil, in which extractable Al was higher than either Clarion or Luther soils yet its affinity coefficient was lower. The relatively low k values obtained for the other two soils (Hayden and Lester soils) could be due to the clay content of these soils.

Figure 3. The effect of pH on Langmuir isotherms for phosphate adsorption by Hayden and Clarion soils. Where (X) is the amount of phosphate-P adsorbed and (C) is P concentration in the equilibrium solution

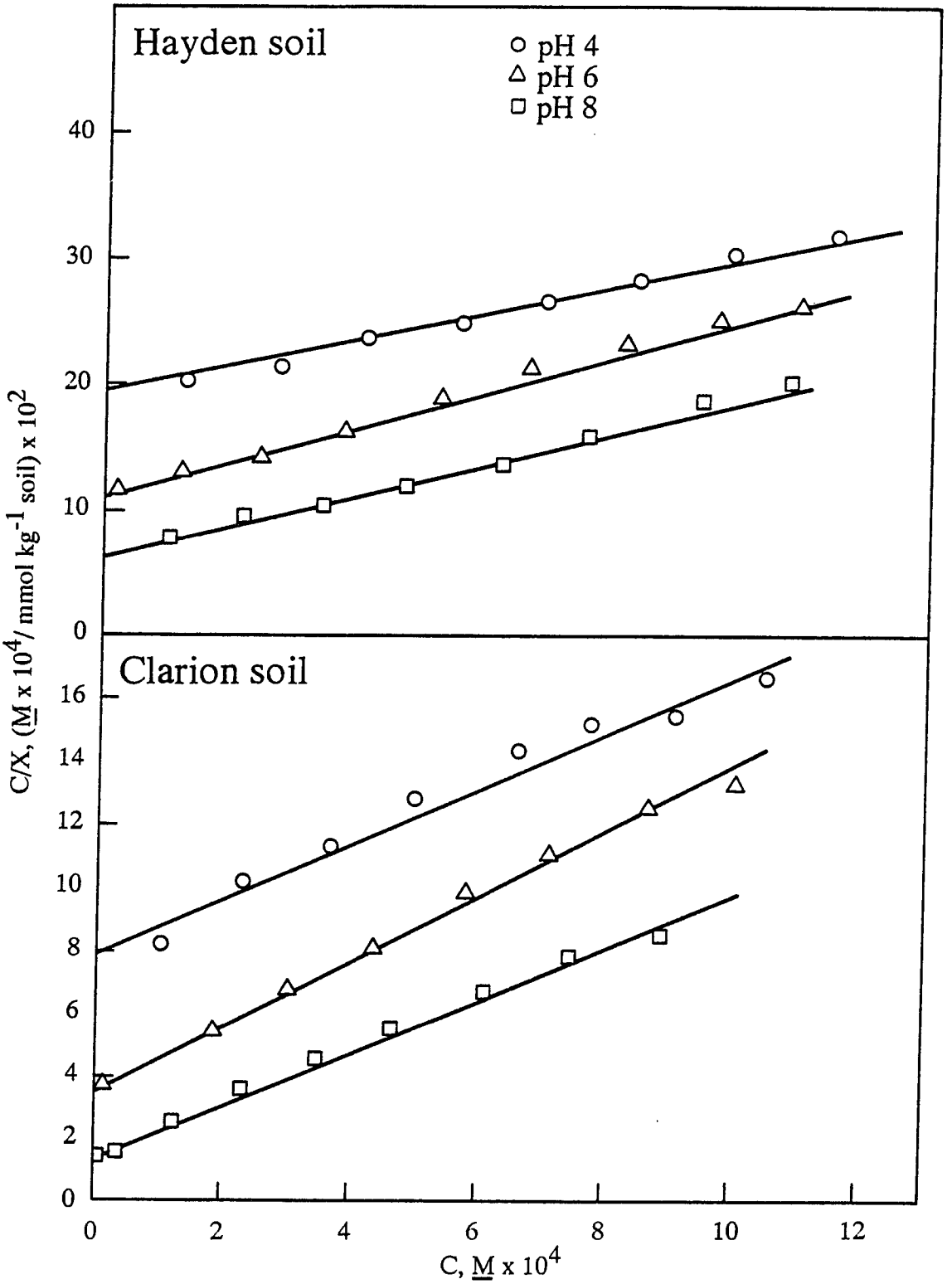

Hayden soil
pH 4
pH 6
pH 8
Clarion soil
C/X, (M x 10^4/ mmol kg^-1 soil) x 10^2
C, M x 10^4
0
2
4
6
8
10
12
14
16
20
30
40

Table 10. Effect of pH on constants of Langmuir isotherms for phosphate adsorption by soils

Soil	pH 4[a]		pH 6		pH 8	
	X_m	k	X_m	k	X_m	k
Hayden	9.93	1.00	7.82	1.06	7.73	2.16
Luther	8.46	1.07	5.96	3.05	5.71	5.66
Tama	11.3	6.80	11.7	8.52	14.4	8.71
Lester	6.49	1.06	5.38	2.07	6.62	3.29
Clarion	11.9	1.04	9.57	3.07	11.6	6.63
Nicollet	9.71	0.37	8.88	1.31	11.5	2.18

[a] X_m, adsorption maximum (mmol P kg^{-1} soil); k, affinity coefficient (reciprocal mmol L^{-1}) calculated from regression equations. All correlation coeffients were >0.917 and were significant at $P<0.01$.

Thus, the results clearly showed the significance of pH on P adsorption by soils. The greatest P adsorption at the highest pH (pH 8) is in contrast to those reported by Hingston (1967, 1972, 1974), Bowden et al. (1980b), and Parfitt (1978) for Al and Fe synthetic oxides. They reported that the highest P adsorption was attained near the pK_1 of the acid H_3PO_4. It is also in contrast to the results of Bolan et al. (1986) for highly weathered acid soils which showed the lowest P adsorption occurred at the highest pH. However, the results reported here (Figures 1 and 2) are in agreement with those reported by MoKwunye (1975) and by White and Taylor (1977) who found that P concentration in soil solution decreased with increasing pH. The

results are also in agreement with those of Murrmann and Peech (1969) and Haynes (1982) who concluded that as the pH increased the labile P and the P in soil solution was generally first decreased, passed through a minimum, and then increased.

The marked differences in the X_m and k values reported in Table 10 for the six soils at pH 4, 6, and 8 could be due to one or more of the factors controlling P adsorption by soils. Among these factors, the mineralization of the organic P, the precipitation of Al polymeric compounds, and the release of P from soil are the most important (Barrow, 1984).

The amounts of P desorbed in five consecutive extractions from Clarion soil as affected by pH (previously equilibrated with 32.3 mmol P kg^{-1} soil) is shown in Figure 4. Similar plots were obtained for other soils. The results obtained for the other five soils are reported in Table 11. The amounts of P adsorbed by these soils varied with pH of the equilibration system, and the highest amount was adsorbed at pH 8. As these results show, the percentages of the adsorbed P desorbed in five consecutive extractions varied among the pH values and soils studied. Although as will be shown the zpc of the soils ranged from 5.0-6.2, the percentage of the desorbed phosphate in four of the soils exceeded 100% at pH 6, suggesting that, in addition to desorption of the adsorbed phosphate, these soils released P from the native adsorbed phosphate or from the hydrolysis of organic P by acid phosphatase. Work by Juma and Tabatabai (1977) showed that acid phosphatase is predominant

Table 11. Effect of pH on the amount of phosphate released from soils previously equilibrated with phosphate solution[a]

Soil	pH[b]	Amount of P adsorbed	Amount of P released with no. of extractions						
			1	2	3	4	5	Total[c]	%[d]
		mmol P kg^{-1} soil							
Hayden	4	4.44	2.81	0.68	0.32	0.17	0.11	4.09	92.1
	6	3.70	2.93	0.65	0.32	0.18	0.15	4.23	114
	8	5.24	3.35	0.89	0.43	0.26	0.21	5.14	98.1
Luther	4	5.45	2.78	0.71	0.33	0.18	0.16	4.16	76.3
	6	3.67	3.12	0.89	0.43	0.25	0.21	4.90	134
	8	8.36	3.64	1.10	0.57	0.34	0.28	5.93	70.9
Tama	4	10.8	4.25	1.76	0.95	0.66	0.50	8.11	75.1
	6	11.1	4.06	1.72	0.96	0.68	0.50	7.92	71.3
	8	12.8	4.52	2.08	1.23	0.89	0.66	9.38	73.3
Lester	4	4.85	3.13	0.68	0.33	0.18	0.13	4.45	91.8
	6	3.52	2.99	0.71	0.31	0.13	0.10	4.24	120
	8	6.64	3.63	0.99	0.52	0.28	0.19	5.65	85.2
Clarion	4	6.39	4.22	1.15	0.46	0.30	0.22	6.35	99.4
	6	6.77	3.98	1.41	0.59	0.44	0.28	6.70	99.0
	8	10.9	4.98	2.11	1.11	0.78	0.56	9.54	85.4
Nicollet	4	4.49	2.72	0.10	0.29	0.27	0.17	3.55	79.1
	6	5.34	3.68	1.14	0.44	0.33	0.15	5.74	107
	8	9.36	4.95	1.79	0.89	0.56	0.30	8.49	90.7

[a]A soil sample (1 g, <2 mm) in a 50-mL plastic centrifuge tube was equilibrated with 25 mL of 0.01 M KCl containing 32.3 μmol of PO_4^{3-}-P at 25°C for 24 h. The soil suspension was centrifuged at 27160 g, and the supernatant was analyzed for PO_4^{3-}. The process of equilibration with fresh solution of 0.01 M KCl but without P (for desorption of the adsorbed P) was repeated for five consecutive times.

[b]The soil:solution pH was adjusted with dilute HCl or KOH to the value indicated before equilibration. The pH values after equilibration did not deviate from the initial values by ±0.2 unit.

[c]Total, total amount of P desorbed, mmol kg^{-1} soil.

[d]Amount of P released expressed as a percentage of total P adsorbed.

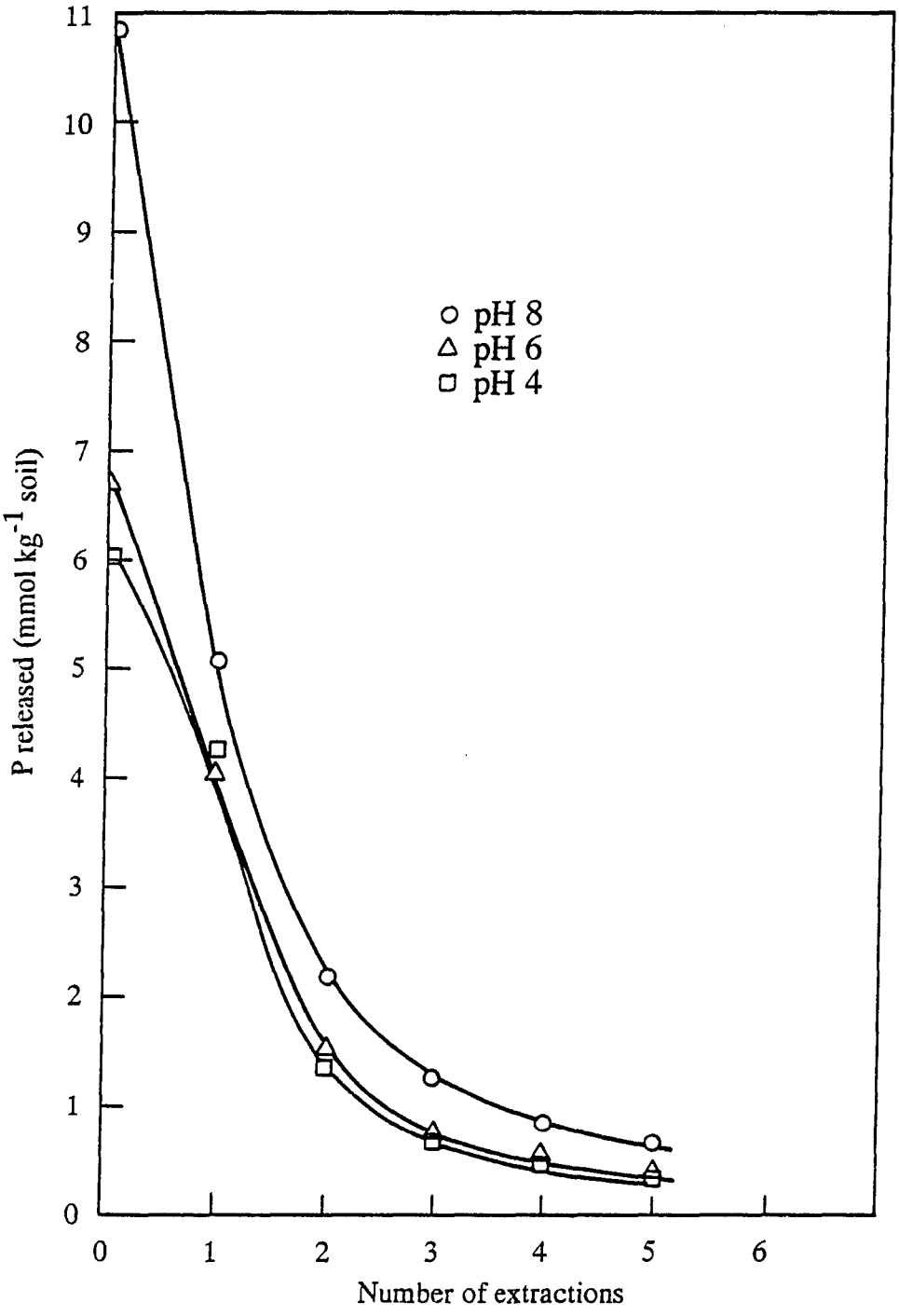


Figure 4. Released of phosphate-P, in sequential extractions with 0.01 M KCl at pH 4, 6, or 8, from Clarion soil treated with 1.29 mmol P kg^{-1} soil

in acid soils with optimum activity at pH 6.5. Therefore, the release of inorganic P from organic sources in soils during the 24 h of equilibration is possible.

The amount of P released by soils as affected by pH values (pH 3-8) of the soil-solution equilibration system are presented in Figure 5. The greatest amount of P released by all the soils examined was at pH 3. This is in agreement with the findings by Barrow (1984) that the release of P is most marked at low pH. The amount of P released at any given pH value differed with soils. The highest amount of P released at pH 3 was by Nicollet soil, which is related, perhaps, to high level inorganic P in this soil. Consequently, this may explain the low affinity coefficient obtained for phosphate adsorption by this soil. At the same time, the lowest amount of P released at pH 3 was with Tama soils, which showed the greatest affinity coefficient for phosphate adsorption.

Some dark-colored organic substances were released from the soils when equilibrated with 0.01 M KCl of pH 8. Organic anions are known to compete with phosphate for adsorption sites (Deb and Datta, 1967a,b; Swenson et al., 1949; Marion and Thomas, 1946; Sinha, 1972). Thus, removing organic compounds at pH 8 perhaps exposed adsorption sites previously occupied by organic anions, and therefore increased phosphate adsorption. The high phosphate adsorption at low pH values is due to its adsorption by Al and Fe hydrous oxides.

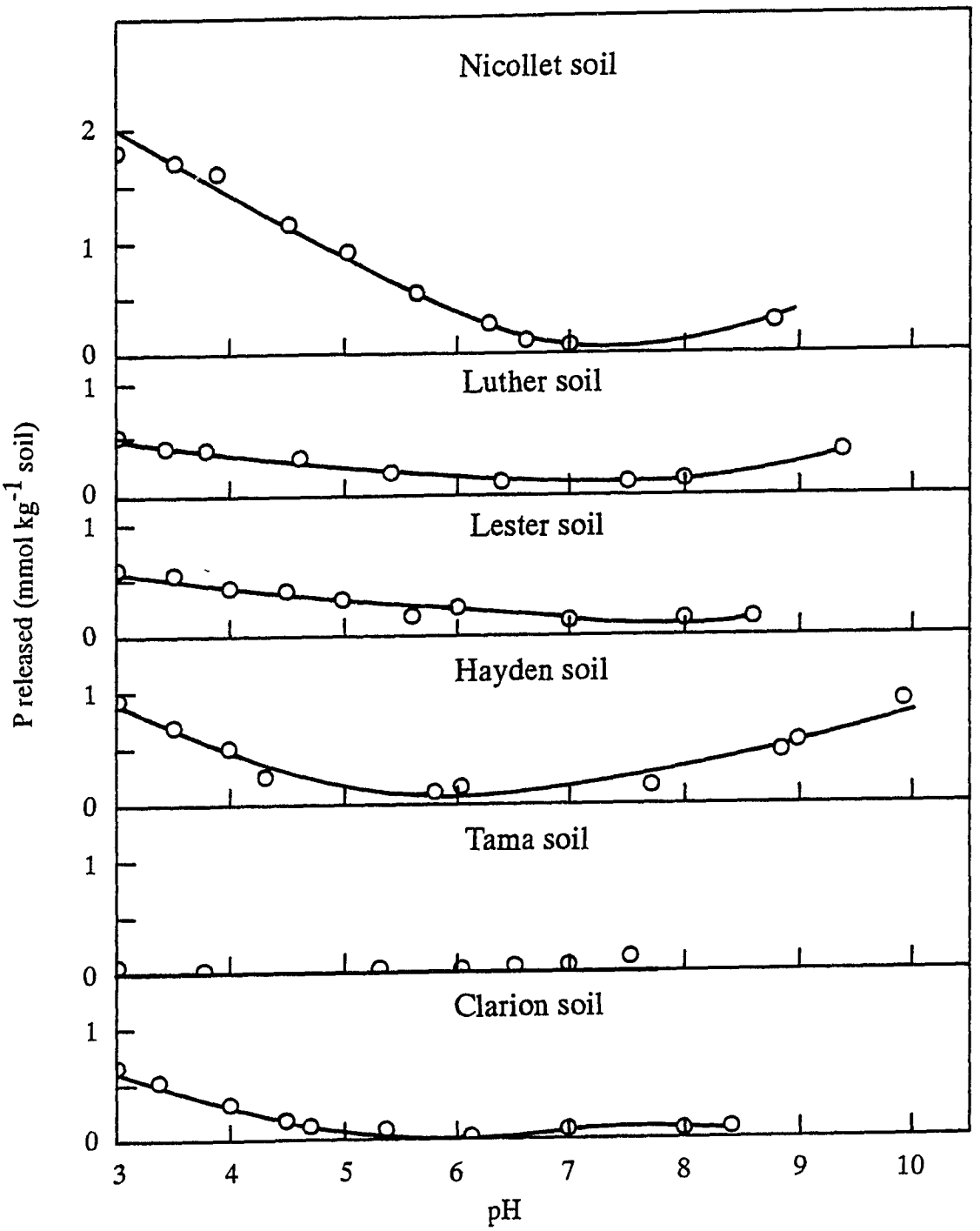
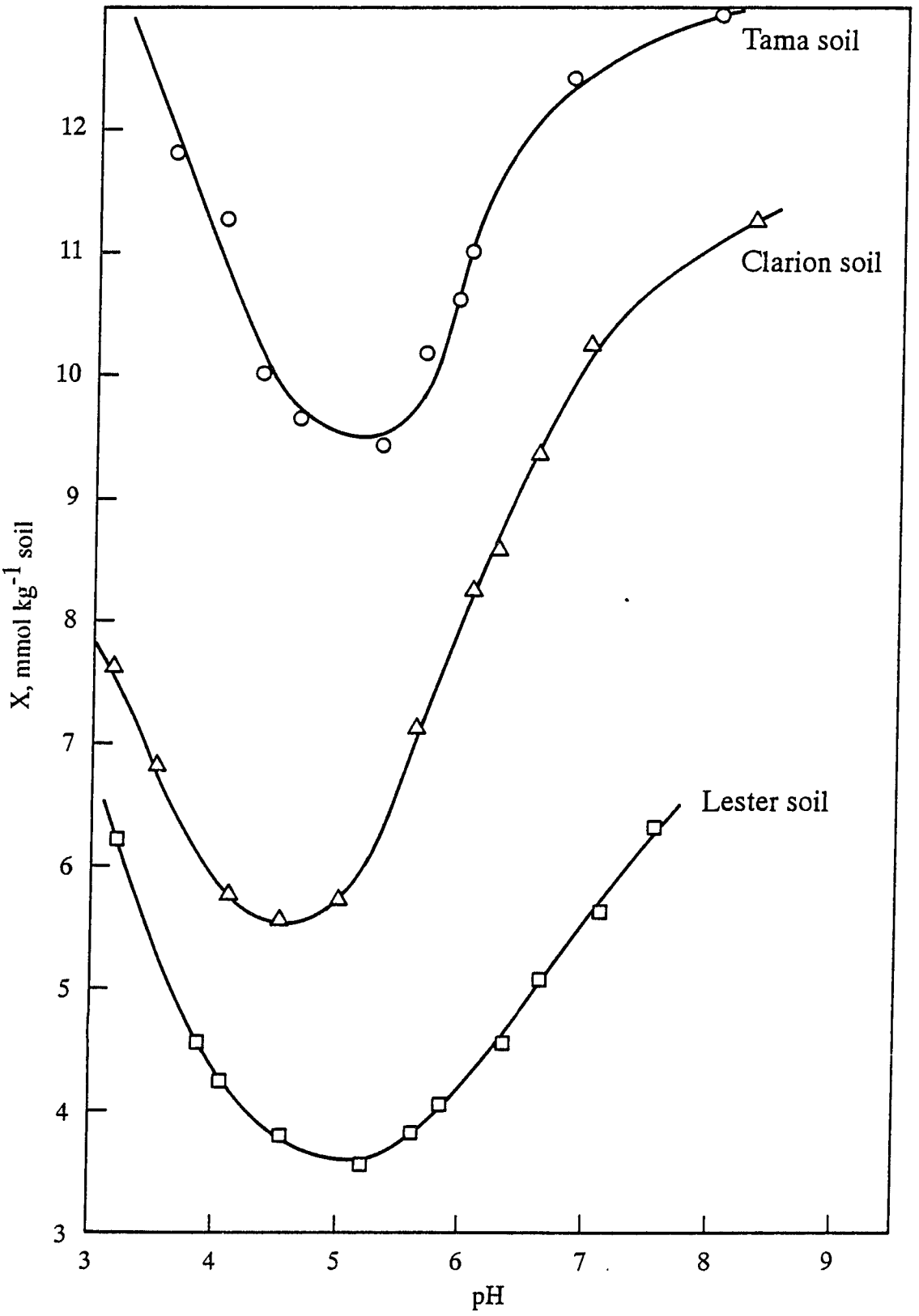


Figure 5. Effect of pH of soil-0.01 M KCl equilibration system on the amounts of phosphate-P released from six Iowa surface soils

To investigate the effect of a wide range of pH values on P adsorption by soils, the P adsorption (X) from a constant amount (1 g of soil was equilibrated with 25 mL 0.01 M KCl containing 1000 μg P) of added P was studied. The amount of P used for this single-point adsorption was selected to allow sufficient adsorption and to minimize the errors associated in calculating the amount of P adsorbed. Amounts of P adsorbed as affected by the pH of the soil:0.01 M KCl-phosphate system (pH 3-8) are presented in Figure 6 for Tama, Clarion, and Lester soils and in Figure 7 for Nicollet, Luther, and Hayden soils. These results show that the amount of P adsorbed varied with the pH, with a minimum adsorption occurring at a narrow zone of pH values (pH 4.5-5.5). The P adsorption increased as the pH increased or decreased beyond this zone of minimum pH. The increase in P adsorption with the decrease in pH (being the greatest at the least pH) is perhaps related to the exchangeable Al and Al and Fe hydrous oxides in the soils. This is in agreement with the findings of Dunbar and Baker (1965), MacKenzie and Amer (1964), and MacKenzie (1962).

The increase in P adsorption with increasing pH (pH 5-8) could be due to the exchangeable cations and anions in soil solution and to a lesser degree to the organic ions. Work by Barrow et al. (1980a) and by Madrid and Posner (1979) showed that at low pH (<zpc) salts decreased the adsorption of P, while at high pH (>zpc) salts increased P adsorption. Determination of zpc of the soils examined showed that zpc values are close to the pH values of minimum P adsorption by soils

Figure 6. Effect of pH of soil-0.01 M KCl equilibration system on the amounts of phosphate-P adsorbed (X) by Tama, Clarion, and Lester soils


Tama soil
Clarion soil
Lester soil
X, mmol kg-1 soil
pH
12
11
10
9
8
7
6
5
4
3
3
4
5
6
7
8
9

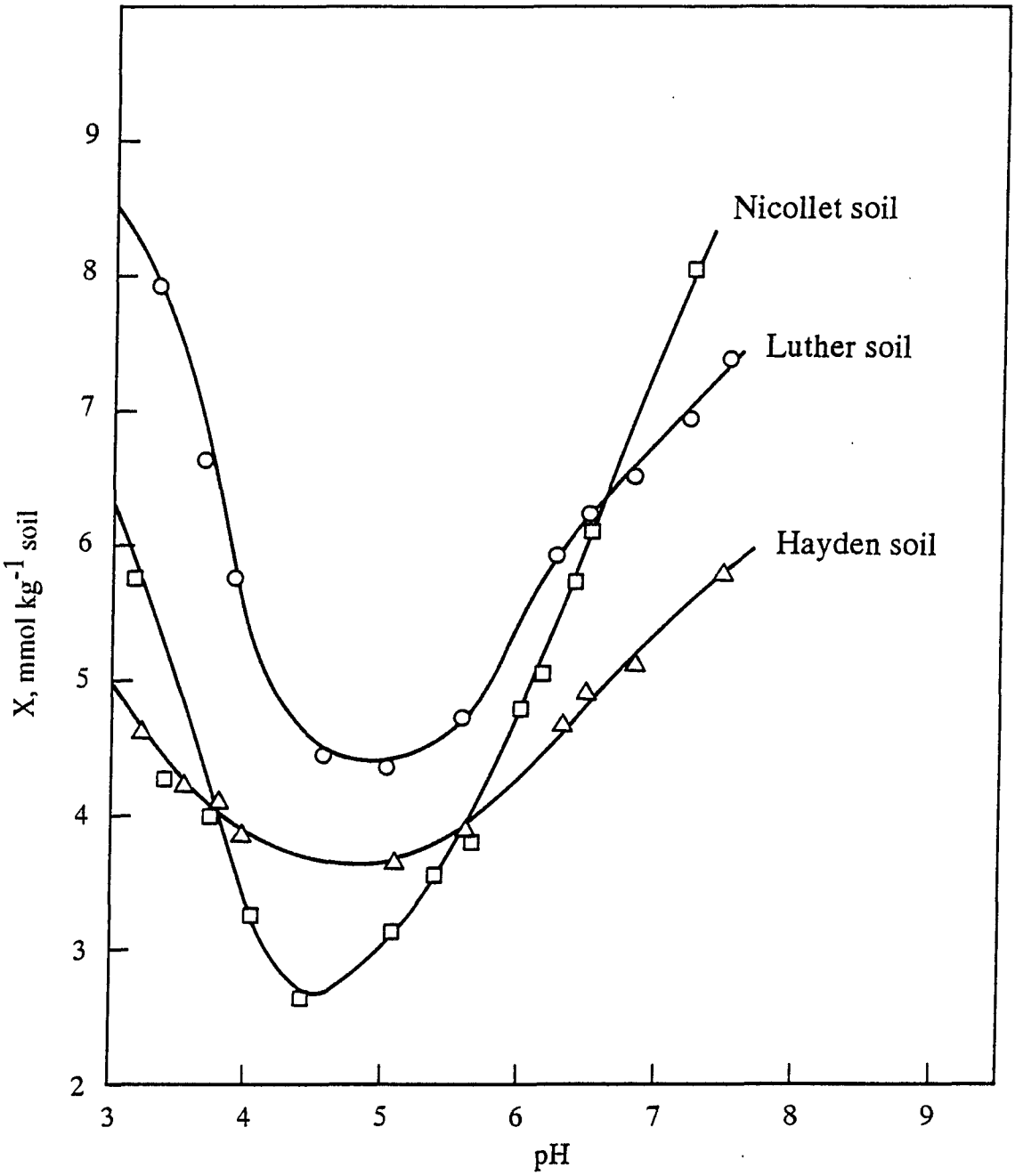


Figure 7. Effect of pH of soil-0.01 M KCl equilibration system on the amounts of phosphate-P adsorbed (X) by Hayden, Luther, and Nicollet soils

(Figures 8 and 9, Table 12). The increase in P adsorption associated with pH values from 5 to 8 could be due to the changes in the ionic strength of the equilibrium solution and to the exchangeable cations in soils. This is supported by the early findings of Teakle (1928), Ravikovitch (1934), and Muljadi et al. (1966a,b) and more recently by Helyar et al. (1976a,b) and Curtin et al. (1987). Thus, the results support the conclusion that pH plays a major role in P adsorption by soils. It may also confirm the importance of the exchangeable cation composition on the P adsorption at near neutral and alkaline pH in the absence of free $CaCO_3$.

To confirm that the exchangeable cations played a role in P adsorption by soils, the exchangeable cations were removed by saturating the soils with NH_4^+. Figures 10 and 11 show that no increase in P adsorption was observed when the soil-0.01 M KCl-phosphate system was adjusted to pH values ranging from 5 to 8 and equilibrated at 25°C for 24 h. As was the case for the results reported in Figures 7 and 8, however, the greatest amounts of P adsorption by the NH_4-saturated soils were obtained at pH 3, suggesting the dominance of Al and Fe hydrous oxides in P adsorption at low pH values.

In saturating the soils with NH_4^+, some organic substances, perhaps organic acids, were removed from the soils. The removal of organic anions during NH_4^+ saturation should leave more vacant adsorption sites for P adsorption at high pH. However, the results presented in Figures 10 and 11 showed that the least P adsorption was at high pH values.

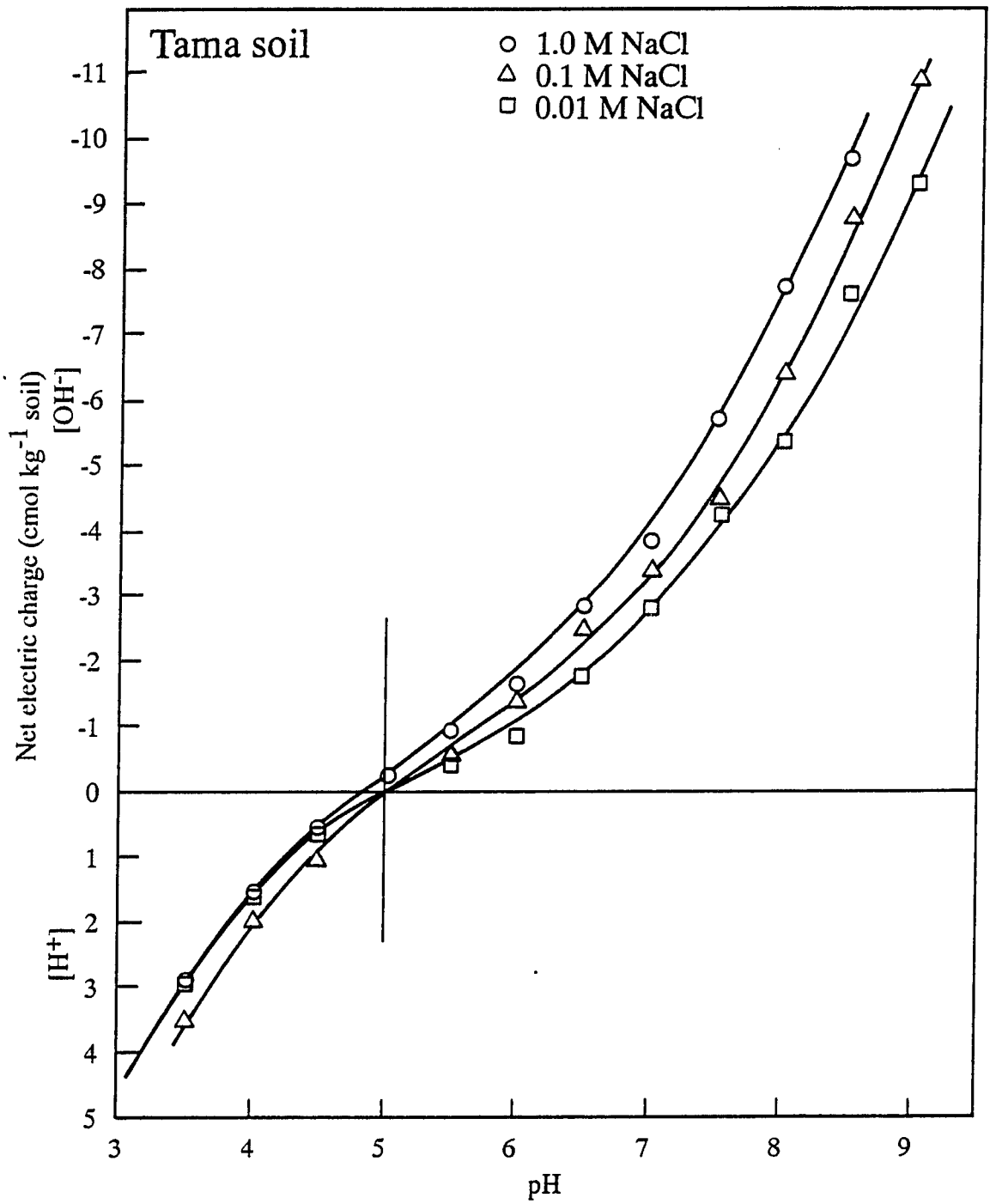


Figure 8. The net electric charge of Tama soil as determined by potentiometric titration

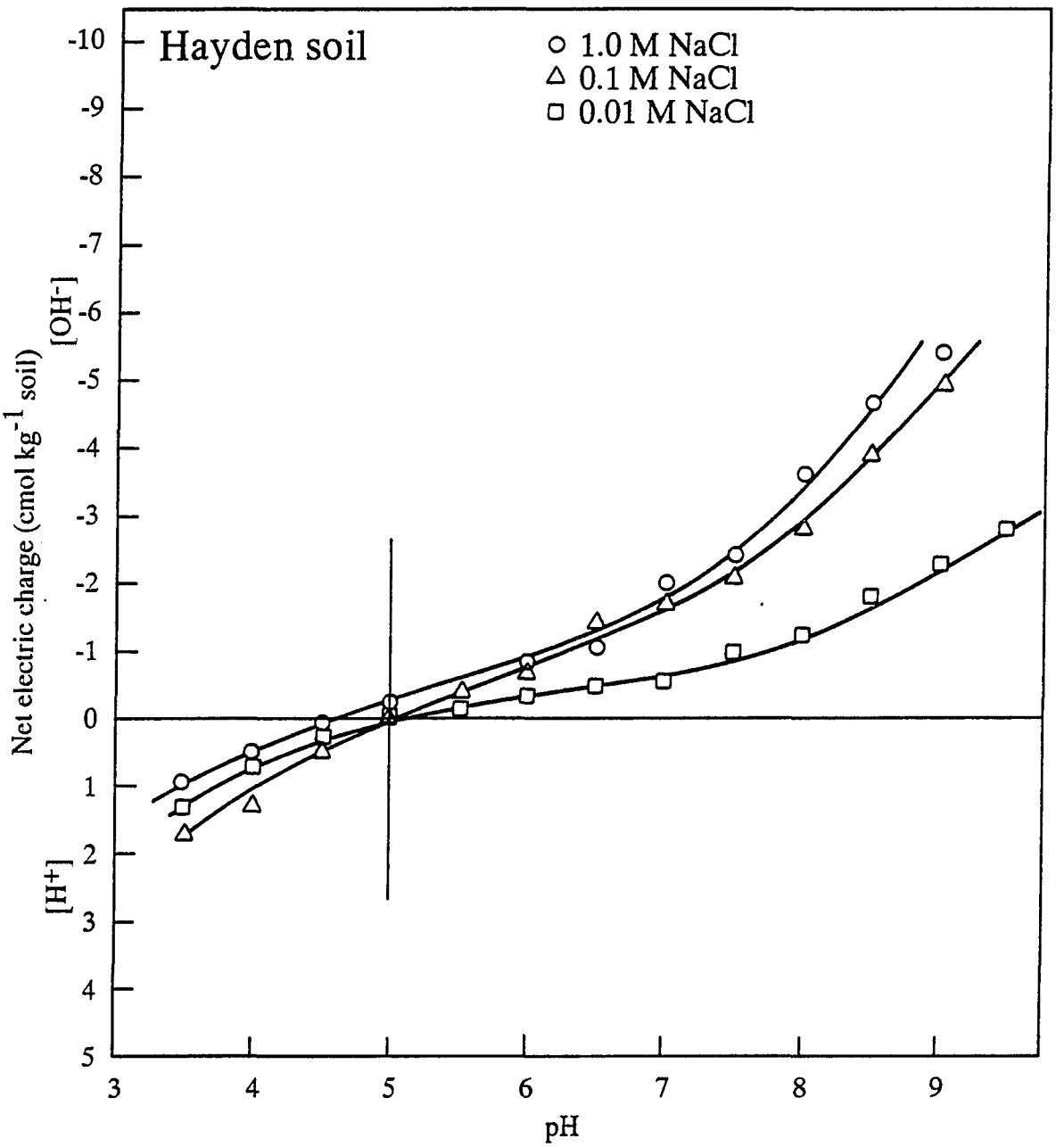


Figure 9. The net electric charge of Hayden soil as determined by potentiometric titration

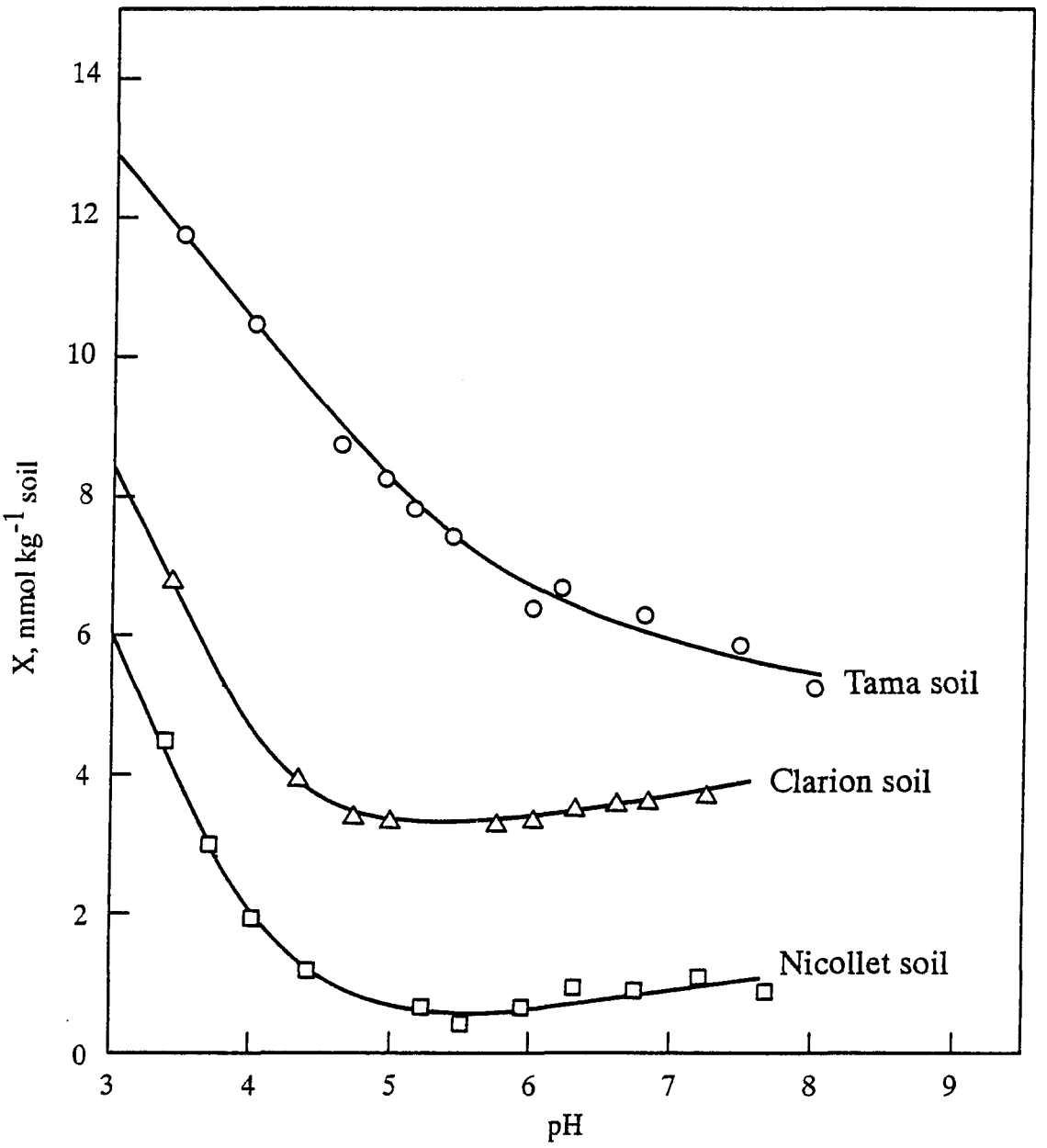


Figure 10. Effect of pH of soil-0.01 M KCl equilibration system on the amounts of phosphate-P adsorbed (X) by NH_4-saturated Tama, Clarion, and Nicollet soils

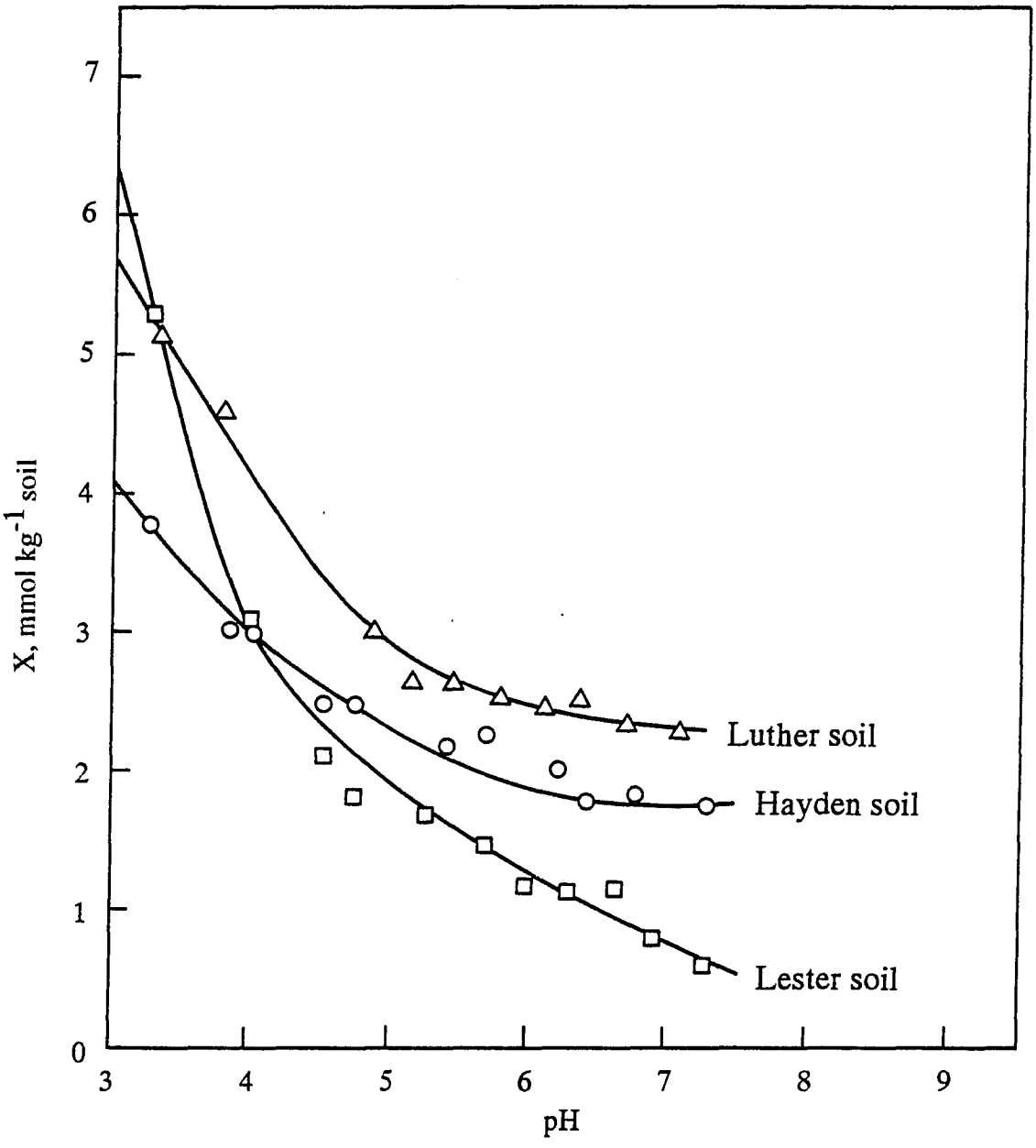


Figure 11. Effect of pH of soil-0.01 M KCl equilibration system on the amounts of phosphate-P adsorbed (X) by NH_4-saturated Hayden, Lester, and Luther soils

Table 12. Zero point of charge (zpc) of the soils studied as determined by potentiometric titration and pH of minimum phosphate adsorption

Soil	zpc	pH_{mpa}[a]
Hayden	5.0	5.0
Luther	5.5	5.0
Tama	5.0	5.0
Lester	6.2	5.0
Clarion	5.3	4.5
Nicollet	5.7	4.5

[a] pH of minimum phosphate adsorption.

The lack of increase in P adsorption by the NH_4-saturated soils at high pH values indicates that no significant numbers of adsorption sites were vacated by the organic compounds removed in the process of NH_4^+ saturation.

PART III. EFFECTS OF LEACHING AND AMMONIUM SATURATION ON PHOSPHATE ADSORPTION BY SOILS

INTRODUCTION

Leaching a soil with water, which simulates soils under heavy rain, may remove soluble salts (ions), some water soluble organic compounds, and some exchangeable cations. However, saturating the exchange sites of the soil with NH_4^+, as is the case with the application of NH_4^+ or NH_4-forming fertilizers, will remove exchangeable cations and part of the organic matter, which become soluble at higher pH (pH>7). As a consequence, these two processes (leaching with water and saturation with NH_4^+) may have important effects on phosphate adsorption by soils. In fact, numerous studies have shown that increasing concentration of nitrate and chloride salts of Ca, Mg, Na, and K increases the adsorption of phosphate by soils, clay, and hydrous oxides of Fe and Al (Kurtz et al., 1946; Clark and Peech, 1960; Fordham, 1963; Jensen, 1970). In addition, many studies have shown that phosphate adsorption by soils vary with the nature of the ionic composition and the ionic strength of supporting matrix solution (Helyar et al., 1976a; Robarge and Corey, 1979; Sims and Ellis, 1983).

Although the effect of exchangeable cations on phosphate adsorption by clay minerals and Al and Fe oxides has been studied by several investigators, little information is available on their effect on phosphate adsorption by soils (Allison, 1943; Chandler, 1941; Ragland and Seay, 1957; Wild, 1953; Pissarides et al., 1968). Recent studies have produced evidence that the equilibrium between surface phosphate and

phosphate in solution is influenced to a considerable degree by the nature of exchangeable cations (Curtin et al., 1987; Smillie et al., 1987; Russell et al., 1988). Results reported in Part II showed that phosphate adsorption increased as pH increased from 6 to 8. This increase in phosphate adsorption was due to the various exchangeable cations in soils, because tests showed that it can be eliminated when the soils were saturated with NH_4^+ (to remove exchangeable cations). Therefore, the work reported in this part was conducted to assess the effects of leaching and ammonium saturation on phosphate adsorption by soils.

DESCRIPTION OF METHODS

Soils

The soils used in this study were Hayden, Luther, Lester, Clarion, and Nicollet. These soils were chosen because of their similarity in pH and because they gave a range in organic matter content and cation-exchange capacity. The pertinent properties of these soils are reported in Table 1, Materials and Methods section.

To remove soluble salts in soils, a soil sample (50 g) in a 1-liter Erlenmeyer flask was treated with 500 mL of deionized water. The flask was stoppered and shaken at 25°C for 24 h. The suspension was filtered (Whatman No. 42 filter paper) and washed three times with 100 ml of water and with 100 mL of isopropyl alcohol in three increments. The soil samples were air dried, crushed to pass a 2-mm sieve, and stored in a glass jar.

To saturate the soil with NH_4^+, a soil sample (50 g) in a 1-liter Erlenmeyer flask was treated with 500 mL of neutral, 1 M NH_4OAc. The flask was stoppered and shaken at 25°C for 24 h. This sample was filtered and washed with dilute NH_4Cl and isopropyl alcohol as described in Part II. The soil sample was air dried and treated as described above for water-leached soils.

Reagents

Stock solutions

Potassium phosphate solution (32.3 mM, 1000 μg P mL^{-1}): One liter of this solution was prepared by dissolving 4.3937 g of KH_2PO_4 in a

1-liter volumetric flask containing about 500 mL deionized water, and the volume was made up with deionized water.

Calcium chloride solution (1 M): One liter of this solution was prepared by dissolving 111 g of $CaCl_2$ in a 1-liter volumetric flask containing about 500 mL deionized water, and the volume was made up with deionized water.

Potassium chloride solution (1 M): One liter of this solution was prepared by dissolving 74.6 g of KCl in a 1-liter volumetric flask containing about 500 mL deionized water, and the volume was made up with deionized water.

Phosphate-working solutions

Ten standard working solutions (0, 0.032, 0.161, 0.323, 0.484, 0.646, 0.807, 0.969, 1.13, and 1.29 mM; i.e., 0, 1, 5, 10, 15, 20, 25, 30, 35, and 40 μg P mL^{-1}) were prepared by adding 0, 1, 5, 10, 15, 20, 25, 30, 35, or 40 mL of the phosphate stock solution to a 1-liter volumetric flask containing 10 mL of 1 M KCl solution and about 500 mL deionized water, and the volume was made up with deionized water. These working solutions were 0.01 M with respect to KCl.

A second set of phosphate working solutions was prepared in $CaCl_2$ by placing 10 mL of 1 M stock $CaCl_2$ solution instead of the KCl solution. The final concentration of $CaCl_2$ was 0.01 M.

A third set of phosphate-working solutions was prepared in deionized water.

Determination of the phosphate adsorption isotherms

Phosphate adsorption isotherms as affected by matrix solutions for the untreated, water-leached, and NH_4-saturated soils were obtained by the same procedures used in studies of the effect of pH on phosphate adsorption isotherms of soils as described in Part II.

Ammonium-N in the filtrates obtained for determination of P was determined on 5-10 mL aliquots by the steam distillation method described by Keeney and Nelson (1982).

RESULTS AND DISCUSSION

The effect of matrix solution on phosphate adsorption isotherms for untreated, water-leached, and NH_4-saturated Hayden, Luther, Lester, Clarion, and Nicollet soils is presented in Figures 12-16, respectively. The matrix solutions used were deionized water, 0.01 M KCl, and 0.01 M $CaCl_2$. Calcium chloride and KCl are the solutions most frequently used by researchers because K^+ and Ca^{2+} are the dominant ions in most soils. Therefore, KCl and $CaCl_2$ solutions may represent the soil solution under field conditions (Rajan and Fox, 1972; Soltanpour et al., 1974). Water was used for comparison because salts in matrix solutions may often lead to over estimation of P-adsorption potential of soils (Singh and Tabatabai, 1976). As indicated by the shape of the adsorption isotherm curves (Figures 12-16), the soil samples were not totally saturated with phosphate (no adsorption plateaus were obtained). The greatest P adsorption by untreated, water-leached, or NH_4-saturated soils occurred when 0.01 M $CaCl_2$ was used as a matrix solution. The greatest phosphate adsorption obtained with $CaCl_2$ is perhaps related to the high ionic strength of this matrix solution (0.025) as compared to that (0.01) of KCl. The greatest P adsorption by soils associated with highest ionic strength is expected because Barrow and Shaw (1979a,b), Helyar et al. (1976a,b), Clark and Peech (1960), Lehr and Van Wesemael (1952), and Posner and Bowden (1980) found that an increase in ionic strength increased phosphate adsorption by soils. It is reported that Ca^{2+}

Figure 12. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Hayden soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$

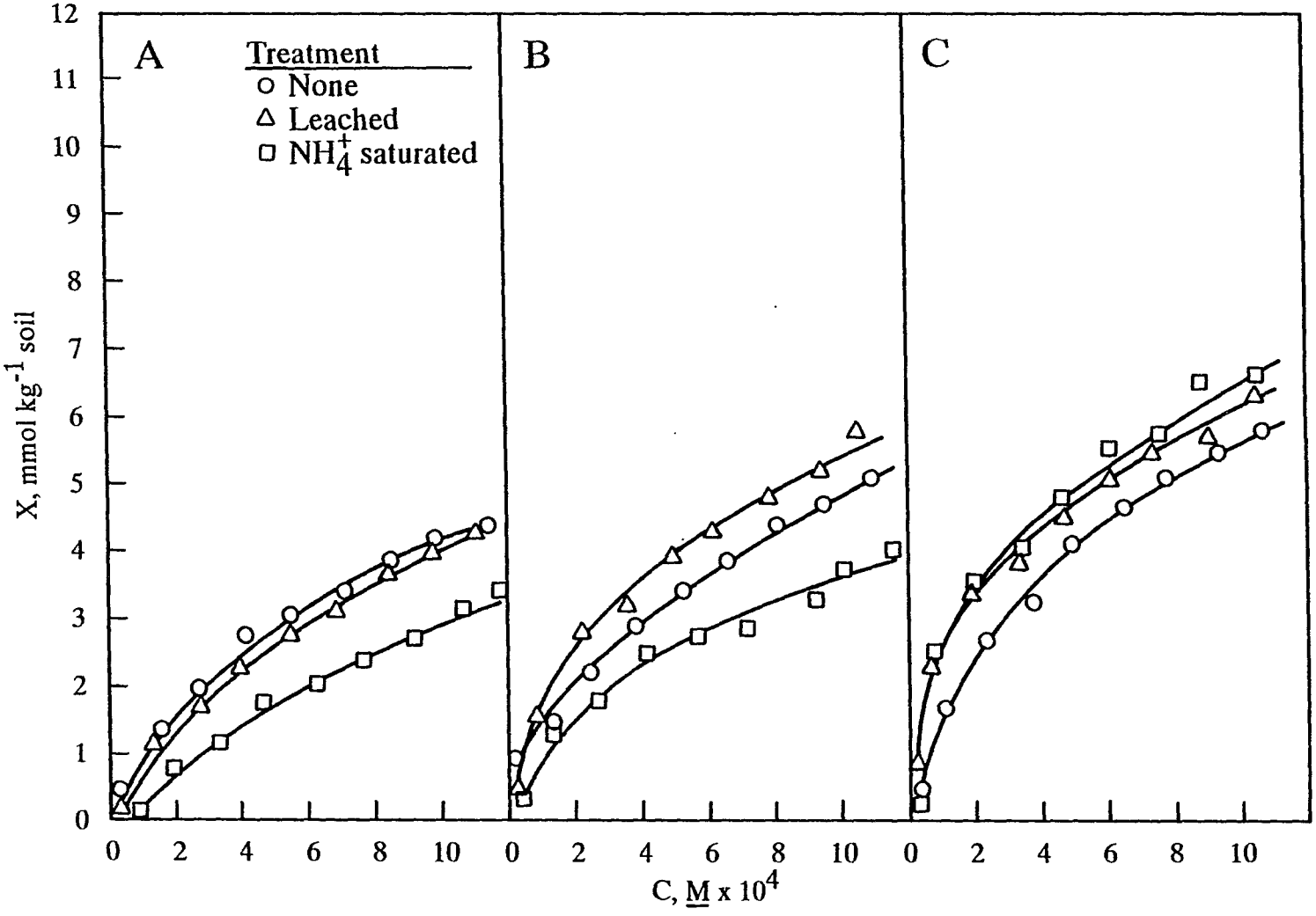

A
B
C
Treatment
None
Leached
NH_4^+ saturated
X, mmol kg^{-1} soil
C, M x 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
0
2
4
6
8
10

Figure 13. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Luther soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$

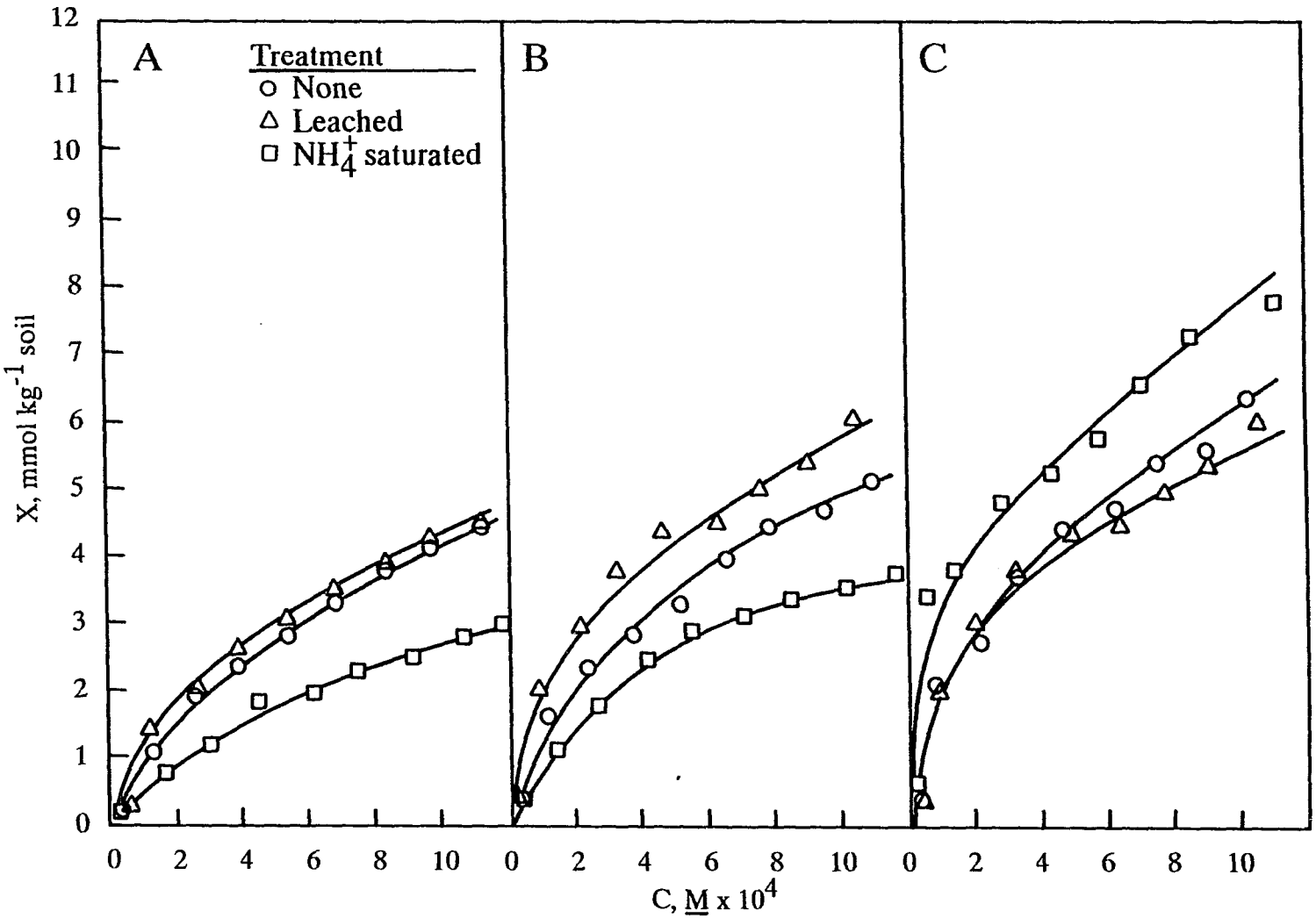

A
B
C
Treatment
None
Leached
NH_4^+ saturated
X, mmol kg^{-1} soil
C, M x 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
0
2
4
6
8
10

Figure 14. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Lester soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$

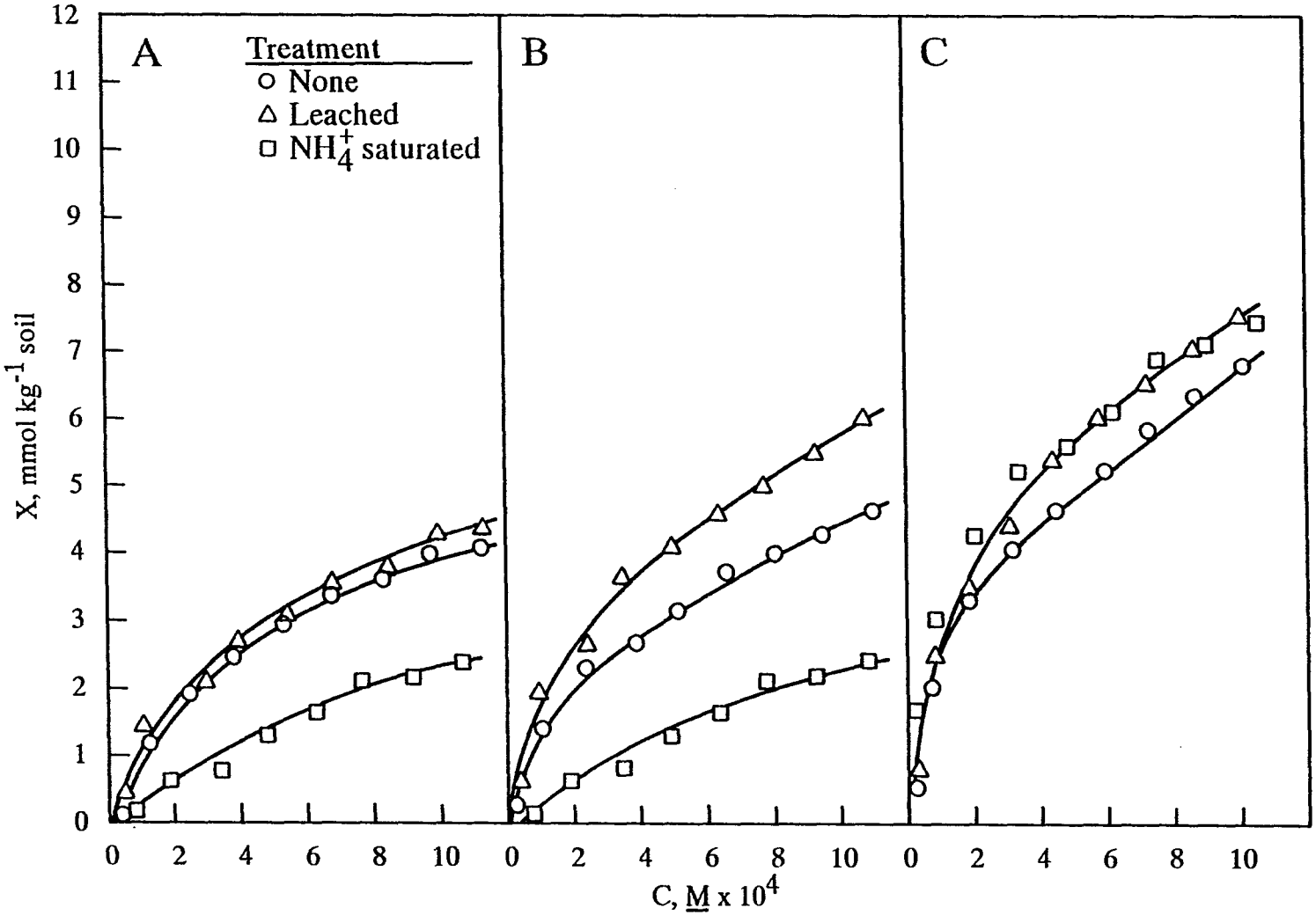

A
B
C
Treatment
None
Leached
NH_4^+ saturated
X, mmol kg^{-1} soil
C, M x 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
0
2
4
6
8
10

Figure 15. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Clarion soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$

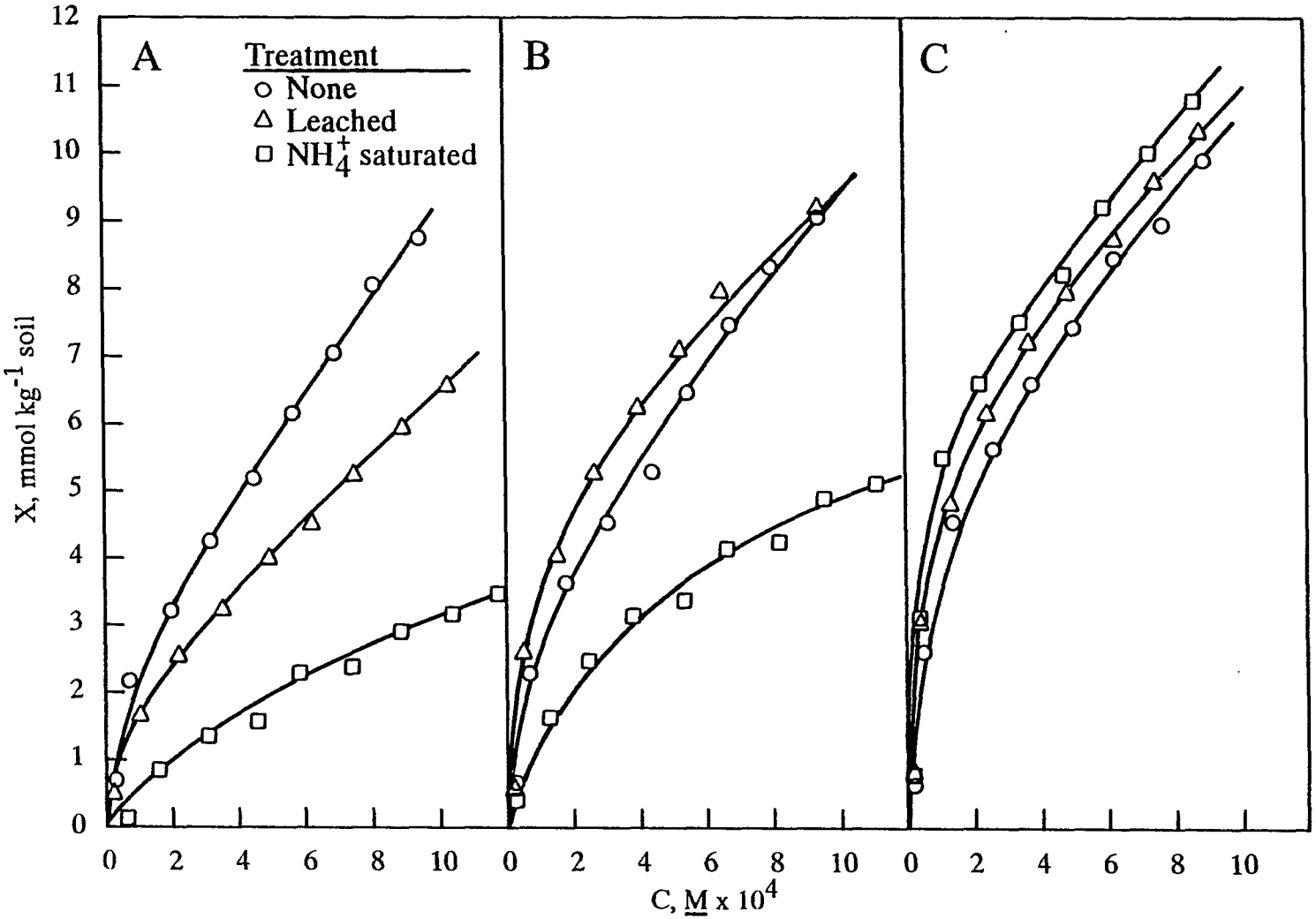
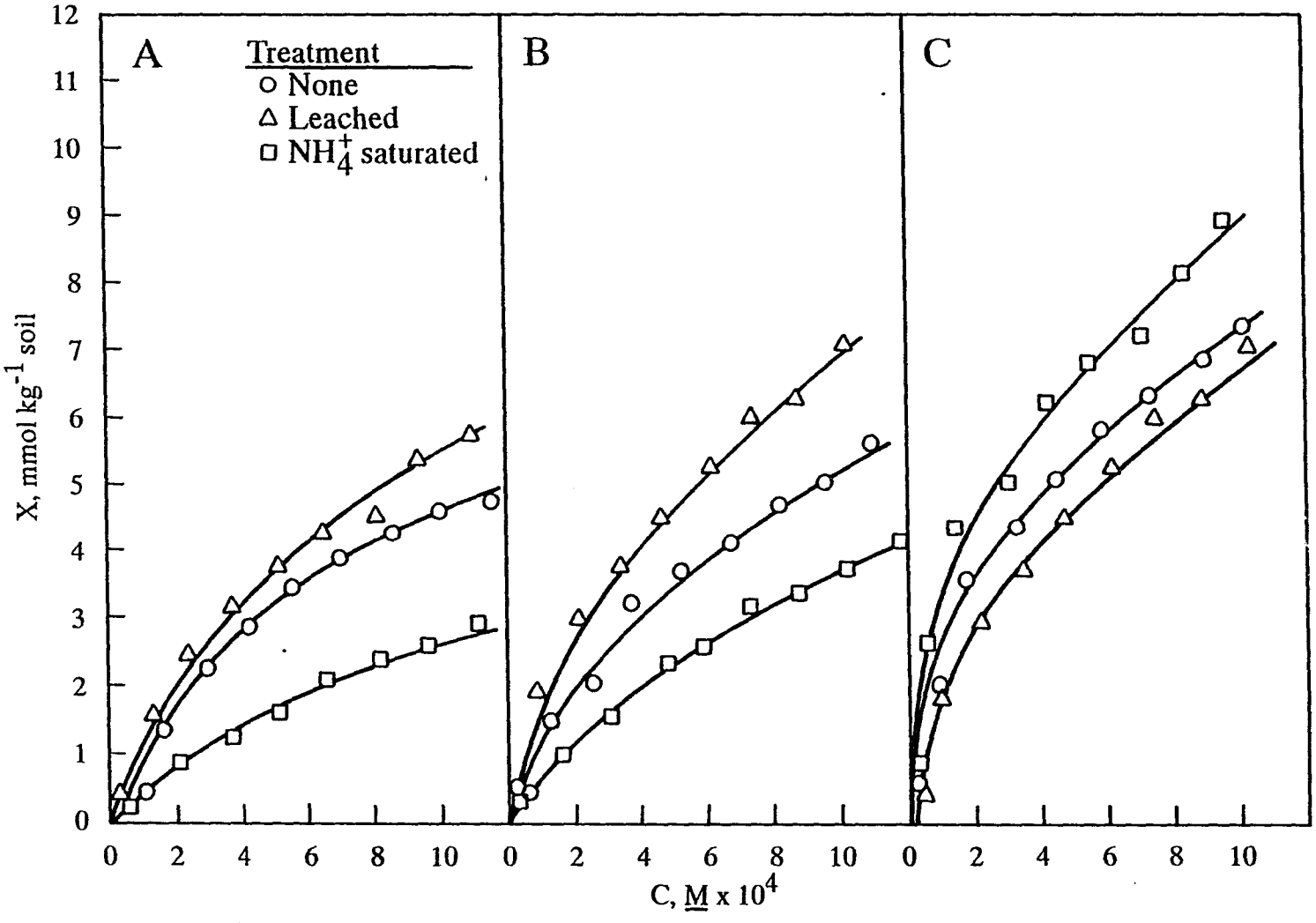

A
B
C
Treatment
None
Leached
NH_4^+ saturated
X, mmol kg^{-1} soil
C, M x 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
0
2
4
6
8
10

Figure 16. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P_+ concentration in the equilibrium solution (C) for Nicollet soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$


A
B
C
Treatment
None
Leached
NH_4^+ saturated
X, mmol kg^{-1} soil
C, M x 10^4
0
1
2
3
4
5
6
7
8
9
10
11
12
0
2
4
6
8
10

increases P adsorption more than other cations (e.g., monovalent cations) because it either complexes with adjacent adsorbed phosphate ions and reduces the repulsion forces between them (Helyar et al., 1976a,b) and/or because Ca^{2+} can be closest to the surface of adsorption (lowest hydroionic diameter), thus reducing the electrostatic potential and increasing P adsorption. These are related to the differences in distribution of electrolytes near the surface of adsorption (Bowden et al., 1977, 1980a).

It is well known that high concentration of NH_4^+ ions have the capability to replace all exchangeable cations of soils (Chapman, 1965). Therefore, equilibration of soils with neutral, 1 M NH_4OAc should remove all the exchangeable cations and convert the soils to monoionic form (i.e., NH_4-saturated soils). The importance of exchangeable cations in P adsorption was demonstrated by the results obtained in the studies of the effect of pH on P adsorption by soils (Part II). As shown in Figures 12-16, phosphate adsorption by NH_4-saturated soils was the least as compared with that by untreated or by water-leached soils when water or KCl was used as a matrix solution. This again confirms the importance of exchangeable cations on P adsorption by soils. However, introducing K ions (when KCl was used as a matrix solution) was not effective in totally offsetting the effect of NH_4 saturation. This is in agreement with the finding of Helyar et al. (1976a) and Robarge and Corey (1979) that phosphate adsorption by soils varies with the nature of the ionic composition of the supporting matrix solution (being greater in

the presence of divalent cations than in the presence of monovalent cations). Introducing K ions resulted in an appreciable increase in P adsorption by most of the soils examined (see A and B in Figures 12-16). This is in contrast to the previous finding by Helyar et al. (1976b) who concluded that, depending on the ionic diameter, the ions that can fit the cavity between two adjacent phosphate ions (hydroionic diameter = 1 A°) can influence P adsorption the most. Potassiums as well as other monovalent ions are not effective in increasing P adsorption by soils because their ionic diameter either exceeds or is much lower than this limit.

When $CaCl_2$ was used as a matrix solution, P adsorption by all soils was the greatest with NH_4-saturated soils (compare C with A and B in Figures 12-16). This considerable increase in P adsorption by the NH_4-saturated soils when Ca^{2+} ions were introduced clearly indicate the effectiveness of Ca^{2+} ions in increasing P adsorption. Determination of the amounts of exchangeable NH_4^+ released to the equilibration solutions when 0.01 M $CaCl_2$ was used as a matrix solution (Table 13) indicated that, in all soils, from 72 to 83% of the exchangeable NH_4^+ was replaced by Ca^{2+}. Thus, it appears that exchangeable Ca^{2+} rather than Ca^{2+} in solution plays a major role in increasing P adsorption by soils.

Although the K ions in 0.01 M KCl matrix solution replaced from 51 to 84% of the exchangeable NH_4^+ ions in all soils and the percentage of replacement varied among soils (Table 13), K^+ was not as effective as Ca^{2+} ions in increasing P adsorption, as indicated by the location

Table 13. Effect of matrix solutions used in constructing phosphate adsorption isotherms on the release of exchangeable NH_4^+ from NH_4-saturated soils

Soil	Percentage of NH_4^+ released from exchangeable NH_4^+ to equilibrium solution specified[a]		
	Water	0.01 M KCl	0.01 M $CaCl_2$
	----------%[b]----------		
Hayden	23.7-43.1	70.9-84.4	79.3-84.9
Luther	19.9-34.9	63.3-67.2	74.3-76.4
Lester	22.7-34.2	52.8-63.1	70.8-77.4
Clarion	18.7-30.4	50.6-55.6	67.2-74.5
Nicollet	22.5-30.6	51.9-56.6	72.1-75.2

[a]NH_4^+ released upon equilibration of soil with a range of phosphate concentrations made either in deionized H_2O, 0.01 M KCl, or in 0.01 M $CaCl_2$ (soil:solution ratio = 1:25). For individual values, see Appendix Table 31.

[b]Percentage of total exchangeable NH_4^+ as determined by extraction with neutral, 1 M NH_4OAc (Chapman, 1965). Ammonium-N in each extract was determined by steam distillation (Keeney and Nelson, 1982).

of the adsorption isotherms (Figures 12-16). The greater effect of Ca^{2+} ion on P adsorption than that of K^+ can be attributed to ion distribution on the adsorption surface as suggested by Bowden et al. (1977, 1980a).

Phosphate adsorption by most water-leached soils when either water or KCl was used as a matrix solution was greater than P adsorption by

untreated or NH_4-saturated soils. This could be due to the removal of a portion of native inorganic, water-soluble P, which in turn led to more vacant P adsorption sites.

When deionized water was used as a matrix solution, the percentage of NH_4^+ released increased with increasing phosphate concentration (Table 13). This is due to the increase in K concentration associated with phosphate, because KH_2PO_4 was used as a source of P. In general, the percentages of NH_4^+ released when water was used as a matrix solution were similar among the five soils used. But these values were lower than those released when 0.01 M KCl or $CaCl_2$ was used as a matrix solution.

The Langmuir adsorption isotherms resulting from the data of P adsorption by Hayden and Clarion soils are shown in Figures 17 and 18, respectively. Similar plots were obtained for P adsorption by the other three soils examined. Plotting the data according to the Langmuir equation was effective in linearizing the data and further illustrating the variations in P adsorption among the soils, treatments, and matrix solutions. The resulting values of adsorption maximum (X_m) and the affinity coefficient (k) for P adsorption by water-leached, NH_4-saturated, and by untreated soils as affected by the matrix solutions are shown in Table 14. The data show that, in general, the X_m values and the k values for untreated, water-leached, or NH_4-saturated soils were the greatest when 0.01 M $CaCl_2$ was used as a matrix solution and the least with water.

Figure 17. Langmuir isotherms for phosphate adsorption by Hayden soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution

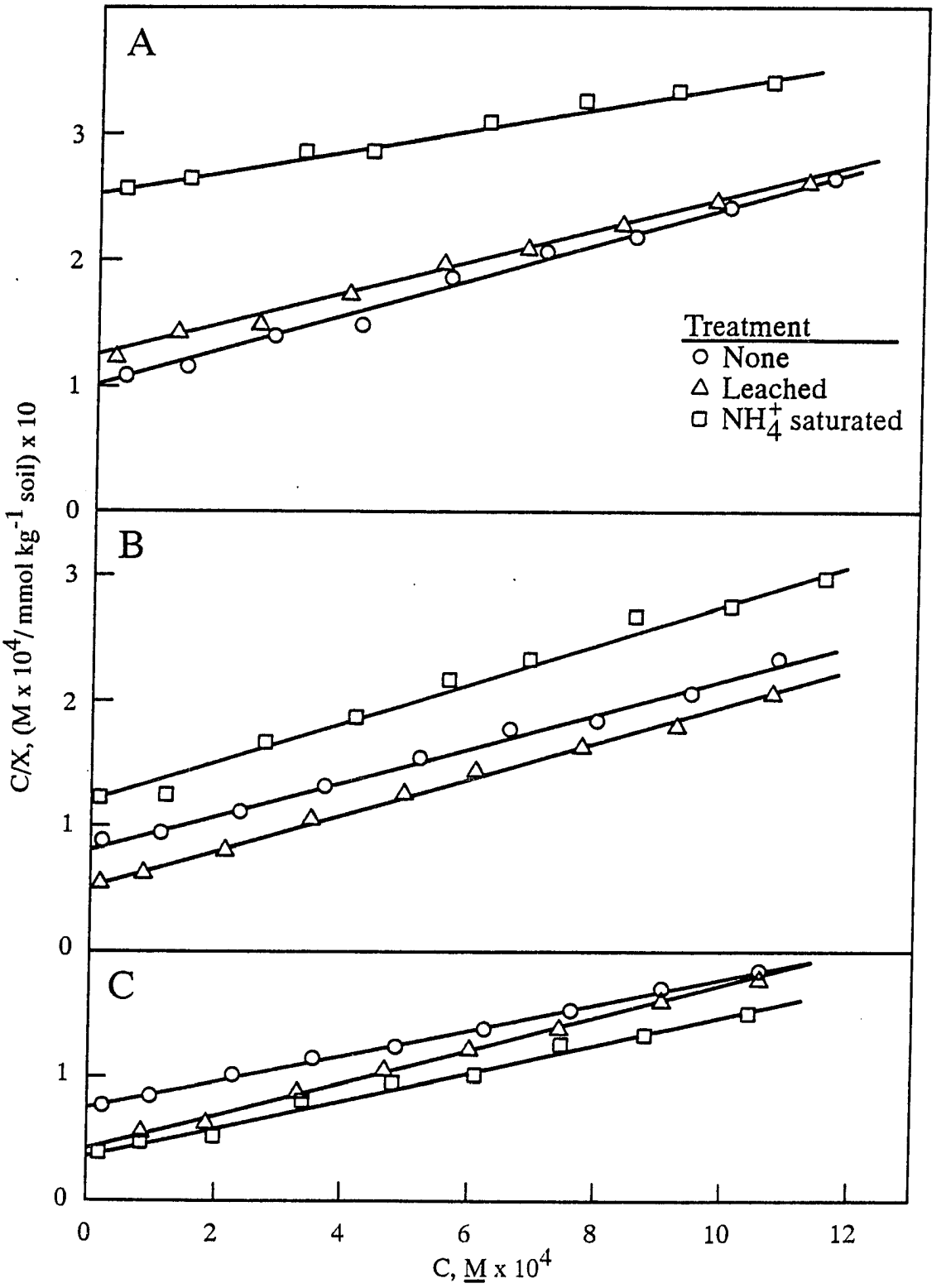

A
B
C
Treatment
None
Leached
NH_4^+ saturated
C/X, (M x 10^4/mmol kg^{-1} soil) x 10
C, M x 10^4
0
1
2
3
4
6
8
10
12

Figure 18. Langmuir isotherms for phosphate adsorption by Clarion soil saturated with NH_4^+ or leached with water as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution

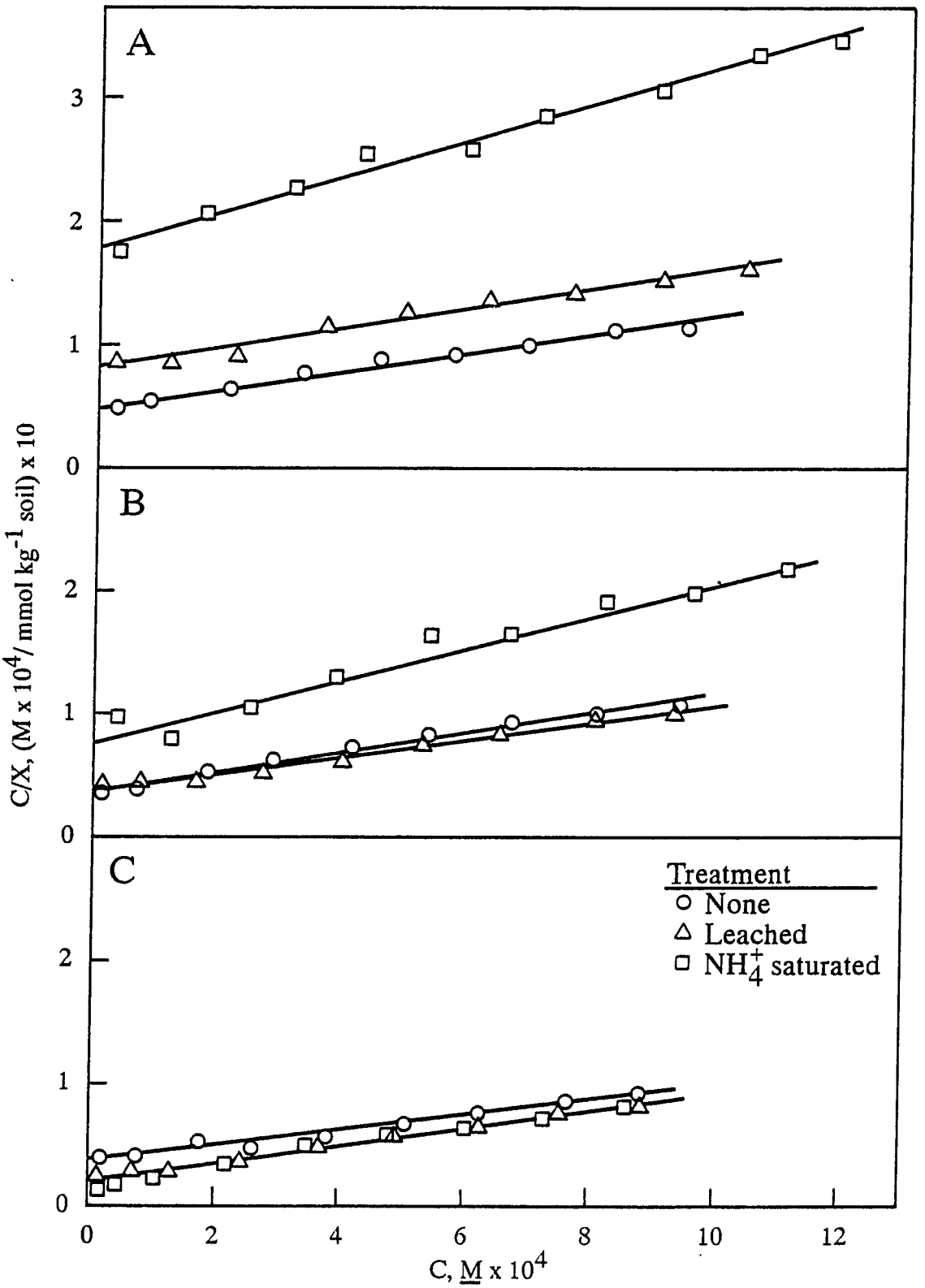

A
B
C
Treatment
None
Leached
NH_4^+ saturated
C/X, (M x 10^4/ mmol kg^{-1} soil) x 10
C, M x 10^4
0
1
2
3
4
6
8
10
12

Table 14. Langmuir constants for phosphate adsorption by untreated, water-leached, and NH_4-saturated soils as affected by matrix solutions

Soil	Treatment[b]	Water[a]		0.01 M KCl		0.01 M $CaCl_2$	
		X_m	k	X_m	k	X_m	k
Hayden	None	6.77	1.52	7.41	1.71	9.71	1.39
	H_2O	7.92	1.00	7.01	2.79	7.38	3.56
	NH_4^+	12.0	0.33	6.09	1.43	8.89	2.74
Luther	None	7.24	1.35	8.18	1.45	8.83	2.14
	H_2O	6.43	1.90	7.61	2.74	8.19	3.70
	NH_4^+	6.62	0.69	5.12	2.19	8.94	4.06
Lester	None	6.19	1.76	6.08	2.45	8.57	3.07
	H_2O	6.33	1.93	8.11	2.09	10.4	2.54
	NH_4^+	6.59	0.54	6.42	1.04	9.21	3.76
Clarion	None	14.1	1.00	12.9	2.15	16.2	1.00
	H_2O	12.1	1.03	13.6	2.16	13.4	3.40
	NH_4^+	7.04	0.78	7.85	1.63	12.0	6.43
Nicollet	None	7.07	1.86	7.23	2.13	10.0	2.56
	H_2O	8.55	1.60	10.6	1.75	10.6	3.34
	NH_4^+	5.76	0.86	9.34	0.69	10.9	3.54

[a] X_m, adsorption maximum (mmol P kg^{-1} soil); k, affinity coefficient (reciprocal mmol L^{-1}).

[b] None, natural (untreated) soil; H_2O, soluble salts were removed by shaking 30 g of soil with 300 mL of deionized water for 24 h and filtering (Whatman No. 42 filter paper); NH_4^+, soil was saturated with NH_4^+.

To assess the effect of matrix solution on pH, the pH of untreated, water-leached, and NH_4-saturated soils was measured in the matrix solutions without P (Table 15). The pH values were the greatest in water and least in 0.01 M $CaCl_2$ solution. For the same soil, the pH was the greatest for NH_4-saturated and least for untreated soils. The low X_m values and the high pH values found for the NH_4-saturated soils (Tables 14 and 15) support the conclusion made in Part II that, at high pH values, exchangeable cations are the dominant factors affecting P adsorption by soils. When water was used as a matrix solution, the X_m values for Hayden and Lester soils were the greatest for the NH_4-saturated soils. This order of X_m in Table 14 is not the same as the location of the P adsorption isotherms (Figures 12-16). This discrepancy could be attributed to the slow reaction rates which followed the rapid initial adsorption reactions (Barrow and Shaw, 1975).

The results showed that X_m values varied among the soils and were affected by soil treatment and the matrix solution used (Table 14). The affinity coefficient (k) values of phosphate adsorption by soils when water was used as a matrix solution was the lowest for the NH_4-saturated soils; however, the k values varied among soils and treatments. Comparison of the effect of matrix solution on P adsorption showed that the k values followed the order: $CaCl_2 > KCl > H_2O$.

Table 15. Effect of NH_4^+-saturation or leaching with water on pH of soils as measured in various aqueous solutions

Soil	Treatment[b]	pH of soil in the presence of aqueous solution indicated[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
Hayden	None	5.50	5.26	4.97
	H_2O	5.06	5.36	5.56
	NH_4^+	7.13	6.76	5.86
Luther	None	5.92	5.73	5.46
	H_2O	5.43	5.72	5.93
	NH_4^+	7.31	6.83	6.78
Lester	None	6.50	6.39	6.10
	H_2O	5.90	6.30	6.38
	NH_4^+	7.31	6.93	5.61
Clarion	None	5.80	5.70	5.36
	H_2O	5.36	5.76	6.00
	NH_4^+	7.14	6.78	5.54
Nicollet	None	6.03	5.84	5.52
	H_2O	5.61	5.98	6.18
	NH_4^+	7.26	6.85	6.68

[a]Soil:H_2O or 0.01 M of either KCl or $CaCl_2$ ratio = 1:25.

[b]None, natural (untreated) soil; H_2O, soluble salts were removed by shaking 30 g soil with deionized water for 24 h and filtering (Whatman No. 42 filter paper); NH_4^+, soil was saturated with NH_4^+ (1 M NH_4OAc) as described by Chapman (1965).

PART IV. EFFECTS OF EXCHANGEABLE ALKALI METALS ON PHOSPHATE ADSORPTION BY SOILS

INTRODUCTION

The alkali metals, Li, Na, K, Rb, Cs, and Fr, which constitute group 1A of the periodic table, differ markedly in soils in regard to their relative abundance, their importance, and their concentration level at which their roles are fulfilled (Scott and Smith, 1987). Of this group of elements, K is the only alkali metal being a major plant nutrient and has been given far more attention than any alkali element in soils. Although Li is not an esential plant nutrient and its soil content is less than 100 mg Kg^{-1} total Li, the importance of Li in soils, however, is related to the fact that little Li can produce a toxic effect in plants (Kabata-Pendias and Pendias, 1984). Many crops benefit by Na (Coughtry et al., 1983, as cited by Scott and Smith, 1987), yet only a few plants seem to require Na. Interest in Rb in soils stems mainly from the potential use of Rb or the radioactive isotope ^{86}Rb as a tracer for K in studies involving soil process and plant uptake (Eckert and McLean, 1980). Limited work has been done on Cs, yet it is more toxic to plants than Rb but less toxic than Li, which may be due to an extremely low level of indigenous Cs in soils.

Effect of alkali metals in soil solution on phosphate adsorption by soils has been investigated in numerous studies (Helyar et al., 1976a; Robarge and Corey, 1979; Kurtz et al., 1946; Clark and Peech, 1960; Fordham, 1963; Jensen, 1970). In general, these studies have concluded that increasing concentration of nitrate and/or chloride salts

of Na and K increase the phosphate adsorption by soils, clay, and hydrous oxides of Fe and Al.

Work by Pissarides et al. (1968) showed that phosphate adsorption maxima, as determined by the Langmuir model for clay minerals (kaolinite, montmorillonite, and illite) saturated with different cations (Li, Na, K, Mg, Ca, Sr, or Ba), were much higher for divalent cations than for monovalent cations, except in the case of K-illite. Also, the release of P from Na-saturated New Zealand soils was found to be four-fold higher than that released from the same original Ca-dominated soils (Curtin et al., 1987). Although these studies have shown that the type of metals on the exchange sites could affect phosphate adsorption, little information is available on the potential effect of individual alkali metals on the exchange sites on phosphate adsorption by soils. Therefore, the objective of the study reported in this part was to evaluate the effect of the alkali metals on phosphate adsorption by soils. To accomplish this objective, five slightly acid Iowa surface soils were saturated with the individual alkali metals (Li, Na, K, Rb, or Cs) and the phosphate adsorption was studied in three matrix solutions (water, 0.01 M KCl, or 0.01 M $CaCl_2$).

DESCRIPTION OF METHODS

Soils

The soils used in this study were Hayden, Luther, Lester, Clarion, and Nicollet. These soils were chosen because of their similarity in pH and because they gave a range in organic matter content and cation-exchange capacity. The pertinent properties of these soils are reported in Table 1, Materials and Methods section.

The soils were converted to monoionic forms by saturating the exchange sites with each of the alkali metals (Li, Na, K, Rb, or Cs). The monoionic soil forms were prepared by the same procedure used in Part II for preparing the NH_4-saturated soils. Because RbCl is expensive ($82/10 g) and not readily available from chemical suppliers, soil:solution ratio = 1:5 was used. A soil:solution ratio = 1:10 was used for the other alkali metals studied. In brief, neutral, 1 M solution of each metal salt (Table 16) was used to saturate the negative sites of the soil and 0.25 M of the metal (in chloride form) was used to leach out the excess solution. Isopropyl alcohol was used to wash out the free solution. Before use, all metal solutions were adjusted to pH 7 with 0.01 M HCl (Table 16). All metal salts used for converting the soils to monoionic forms were Fisher certified reagent chemicals (Fisher Scientific Company, Itasca, IL).

The pH (soil:solution ratio, 1:25) of the alkali metal-saturated soil was determined in water, 0.01 M KCl, and 0.01 M $CaCl_2$ by using a glass electrode.

Table 16. Alkali metal salts used in converting soils to monoionic forms

Alkali metal	Alkali metal salt used	Formula weight	Concentration[a] M	pH[b]
Li	LiCl	42.4	1.0	8.35
Na	$NaC_2H_3O_2$	82.0	1.0	7.81
K	$KC_2H_3O_2$	98.2	1.0	8.74
Rb	RbCl	120.9	1.0	9.12
Cs	$CsC_2H_3O_2$	191.7	1.0	8.48

[a]Prepared in deionized water.

[b]The formula weight was dissolved in about 600 mL of deionized water, and the solution was titrated to pH 7.0 with 0.1 M HCl before adjusting the volume to 1 L.

The exchangeable alkali metal of the metal-saturated soil was extracted with neutral, 1 M NH_4OAc (1 g soil + 25 mL NH_4OAc in 50-mL plastic centrifuge tube); the mixture was shaken for 24 h, centrifuged at 27160 g, and the supernatant was transferred into a 100-mL volumetric flask. The soil residue was washed three times with 25 mL of neutral, 1 M NH_4OAc, mixed thoroughly and centrifuged, and the supernatants were combined. The volume was adjusted to 100 mL with neutral NH_4OAc, and the alkali metal was determined by atomic absorption spectroscopy (Perkin-Elmer Model 5000).

Reagents

Stock solutions

The stock solutions needed for this study were prepared as described in Part III. These were 32.3 m$\underline{M}$ KH_2PO_4, 1 $\underline{M}$ KCl, and 1 $\underline{M}$ $CaCl_2$.

Phosphate-working solutions

The 10 standard working solutions used in Part II were used in this study. These standard solutions were made in water, 0.01 $\underline{M}$ KCl, and 0.01 $\underline{M}$ $CaCl_2$ as described in Part III.

Determination of the phosphate adsorption isotherms

Phosphate adsorption isotherms for the alkali metal-saturated soils, as affected by matrix solutions, were constructed as described in Part II for the effect of pH on phosphate adsorption.

Alkali metals released from the metal-saturated soils to the matrix solution during equilibration of soil with the range of P concentrations, used to construct the adsorption isotherms, were determined in the clear filtrate used to determine the P remaining in the equilibrium solutions. Sodium and K were determined by atomic emission spectrophotometry (Instrumentation Laboratory, Flame Photometer Model 443), while other alkali metals were determined by atomic absorption spectrophotometry (Perkin-Elmer Model 5000).

RESULTS AND DISCUSSION

Phosphate adsorption isotherms for alkali metal-saturated Hayden, Luther, Lester, Clarion, and Nicollet soils as affected by the matrix solutions are presented in Figures 19-23, respectively. The amount of P adsorbed by soils, as indicated by the location of adsorption isotherms, increased nonlinearly with concentration of P in solution. These figures also illustrate the considerable variations in the amount of P adsorbed as affected by saturating soils with different alkali metals. In general, all isotherms showed a diminishing rate of increase in the amount of P adsorbed with increasing equilibration P concentration.

The amounts of P adsorbed by soils saturated with alkali metal were affected by the matrix solutions (i.e., water, 0.01 M KCl, or 0.01 M $CaCl_2$) used. The isotherm curves show that the amount of P adsorbed by the soils at any phosphate concentration in equilibrium solutions was much higher when 0.01 M $CaCl_2$ than when either water or 0.01 M KCl was used as a matrix solution. However, the amount of P adsorbed when water was used as a matrix solution was much lower than when 0.01 M KCl was used as a matrix solution. Furthermore, when water was the matrix solution, P adsorption by untreated soils was much greater than P adsorption by metal-saturated soils. The least P adsorbed, however, was exhibited by soils saturated with Na (Figures 19-23, A). This supports the finding of Curtin et al. (1987), who concluded that saturation

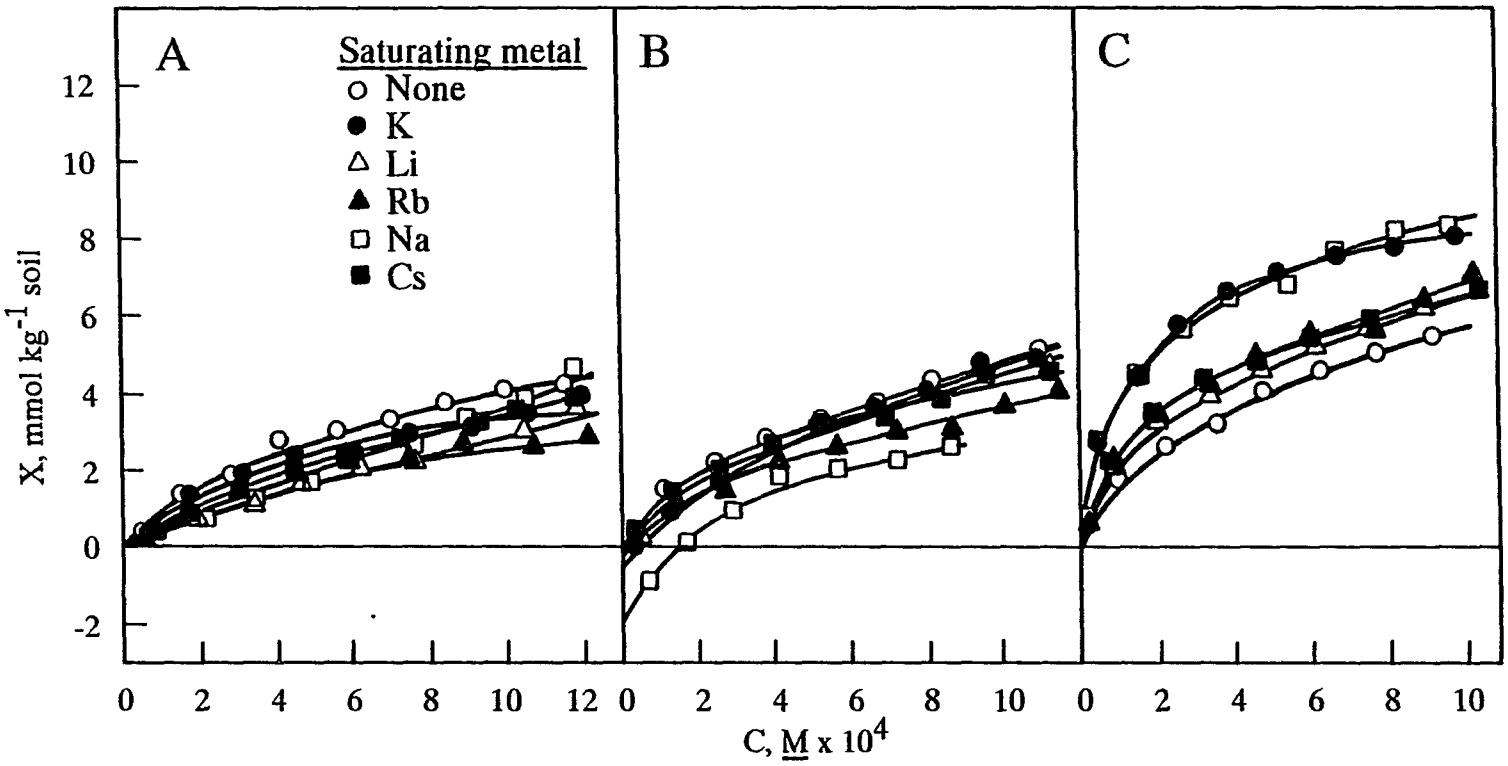


Figure 19. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in equilibrium solution (C) for Hayden soil saturated with Li, Na, K, Rb, or Cs as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

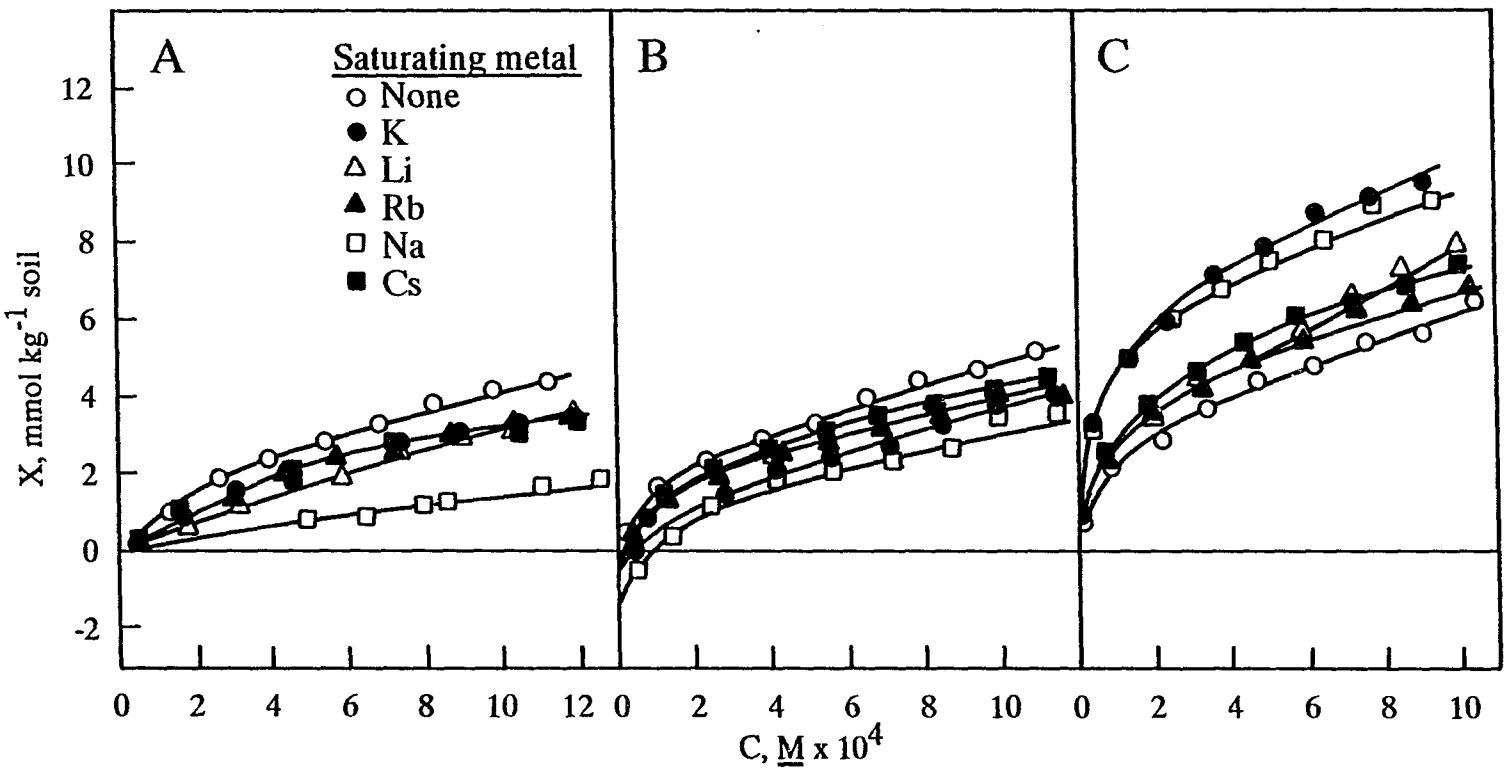


Figure 20. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in equilibrium solution (C) for Luther soil saturated with Li, Na, K, Rb, or Cs as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

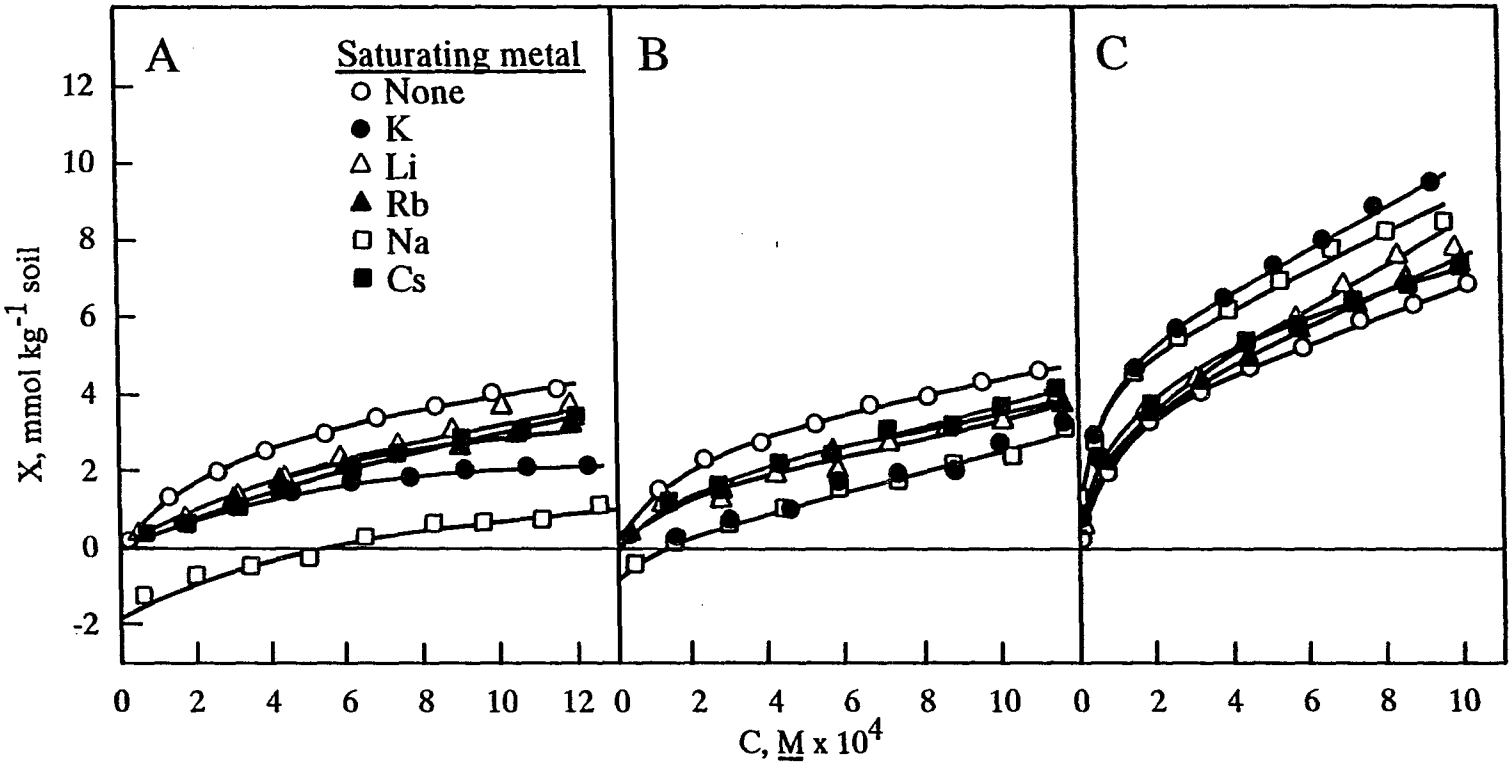


Figure 21. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in equilibrium solution (C) for Lester soil saturated with Li, Na, K, Rb, or Cs as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

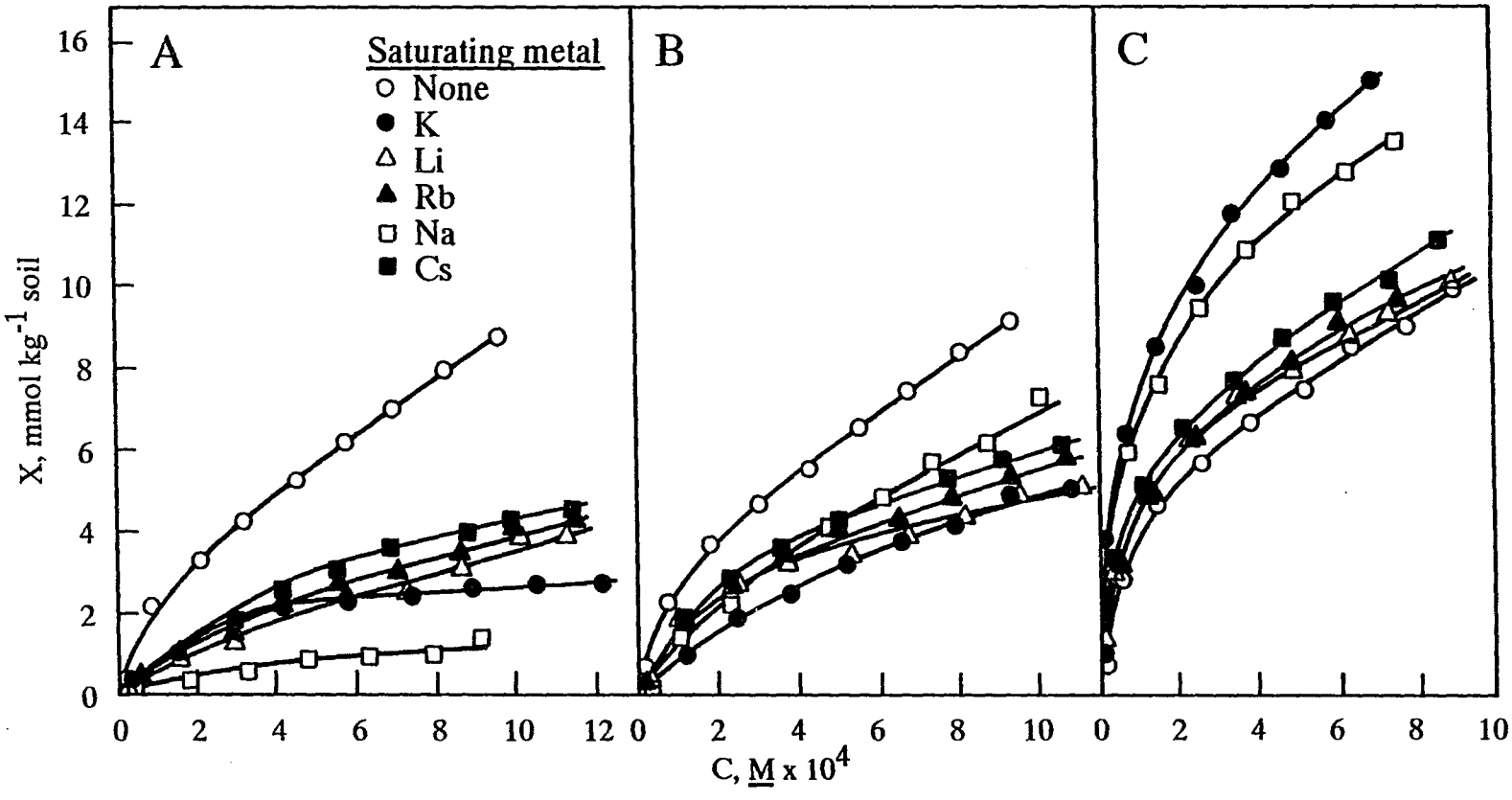


Figure 22. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in equilibrium solution (C) for Clarion soil saturated with Li, Na, K, Rb, or Cs as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

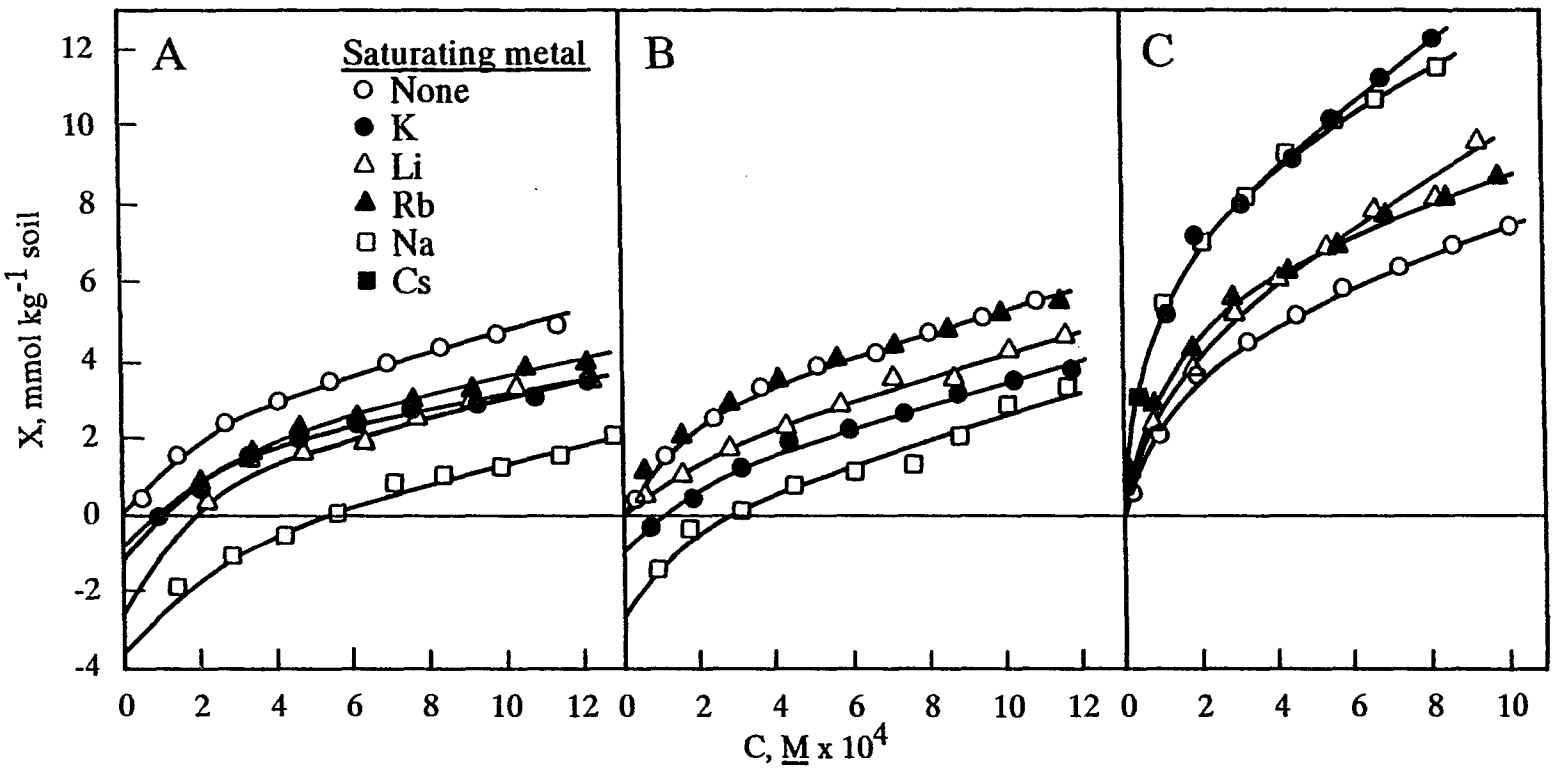


Figure 23. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in equilibrium solution (C) for Nicollet soil saturated with Li, Na, K, Rb, or Cs as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

of soils with Na increased the release of P up to four-fold over that of the original Ca-dominated soils. Also, it is in agreement with findings of Russell et al. (1988), Smillie et al. (1987), and Sharpley et al. (1988). All reported that P release by soils increased with increase in Na-saturation.

It is noteworthy to note that Lester and Clarion soils saturated with Na, K, and Li exhibited a small negative adsorption of P when water was used as a matrix solution. This negative adsorption may be related to either high native P in these two soils, as reported in Table 1, and/or to mineralization of organic P.

The use of 0.01 M KCl as a matrix solution resulted in relatively larger amounts of P adsorbed at any given P solution concentration than when water was used as a matrix solution, as shown by comparing A and B of Figures 19-23. The greatest amount of P adsorbed was obtained with untreated soils and the least with Na-saturated soils, as was the case when water was used as a matrix solution, in spite of introducing K^+ ions. However, at low P concentrations, phosphate release rather than adsorption was exhibited by all soils except with Clarion soil. This appreciable release of P changed to adsorption at high P concentration in the equilibration solution.

By using $CaCl_2$ as a matrix solution for P adsorption by alkali metal-saturated soils, results showed that the amount of P adsorbed followed the order: $K \geq Na > Rb > Cs > Li >$ untreated soils. The amounts of P adsorbed by soils saturated with Na or K was the greatest

when $CaCl_2$ was used as a matrix solution, and it was the least when either water or KCl was used as a matrix solution (Figures 19-23). There are at least two possible reasons to explain these differences in P adsorption by the soils when saturated with Na or K. One reason is that the amount of organic compounds solubilized from alkali metal-saturated soils during equilibration with phosphate varied with the alkali metal used (indicated by the color of the soil extracts). This was especially true when the soils were saturated with Na and water was used as a matrix solution. Less colored organic compounds were released to the equilibrium solution when KCl was used; and very little, if any, colored organic substances were released when 0.01 M $CaCl_2$ was used as a matrix solution.

The other reason for the difference in P adsorption when the soils were saturated with Na or K and equilibrated in $CaCl_2$ is that Na^+ and K^+ are effectively saturated at all the exchange sites as determined by replacements with NH_4^+ ions. Table 17 shows the apparent cation-exchange capacity of the five soils determined by using NH_4OAc or alkali metal salt solutions. Results showed that, in general, Na^+ and K^+ ions gave about the same CEC values as did NH_4^+ as a saturating ion. However, the other alkali metals used (Li, Rb, Cs) may be as effective as K^+ and Na^+ in saturating the exchange sites but may not be as easy to replace by NH_4^+ as Na^+ or K^+. These apparent differences in the degree of saturation of soils by different alkali metals may be related to either specific interaction of these metals (Li, Rb, and Cs) with

Table 17. Cation-exchange capacity of soils as determined by using NH_4OAc or alkali metal salt solutions

Saturation ion[b]	CEC of soil indicated[a]				
	Hayden	Luther	Lester	Clarion	Nicollet
	cmol (+) kg^{-1} soil				
NH_4^+	10.5(100)	14.0(100)	19.5(100)	25.9(100)	25.8(100)
Li^+	6.3(60.0)	8.6(61.4)	12.9(66.2)	14.3(55.2)	14.8(57.4)
Na^+	11.0(105)	14.0(100)	19.0(97.4)	24.0(92.7)	25.0(96.9)
K^+	11.0(105)	12.3(87.9)	18.1(92.8)	24.4(94.2)	24.9(96.5)
Rb^+	8.9(84.4)	11.4(81.4)	17.9(91.8)	24.5(94.6)	ND[c]
Cs^+	5.86(55.8)	8.84(63.1)	14.7(75.4)	18.9(73.0)	18.6(72.1)

[a]Figures in parentheses are CEC values expressed as percentages of the values obtained by using neutral, 1 M NH_4OAc.

[b]Soil sample (10 g, <2 mm) was treated with 250 mL neutral, 1 M NH_4OAc or neutral, 1 M alkali metal solution indicated in Table 16. After shaking for 24 h, the suspension was filtered (Whatman no. 42 filter paper) and washed five times with 0.1 M of the corresponding salt solution and finally with 250 mL of isopropyl alcohol. When NH_4^+ was used as a saturating ion, the soil was air-dried for use in the studies of phosphate adsorption. Exchangeable alkali metal of the metal-saturated soil was extracted with neutral, 1 M NH_4OAc (1 g soil + 25 mL NH_4OAc in a 50-mL plastic centrifuge tube); the mixture was shaken for 24 h, centrifuged at 27160 g and the supernatant was transferred into a 100-mL volumetric flask. The soil residue was washed three times with 25 mL of neutral, 1 M NH_4OAc, mixed thoroughly and centrifuged, and the supernatants were combined. The volume was adjusted to 100 mL with neutral, 1 M NH_4OAc, and the alkali metal was determined by atomic absorption spectroscopy.

[c]Not determined.

soils or may be related to interlayer fixation as in the case of K-illite (Pissarides et al., 1968). Thus, P adsorption by soils saturated with either Li^+, Rb^+, or Cs^+ was less than when saturated with either Na^+ or K^+ metal and equilibrated in $CaCl_2$ as a matrix solution. The reverse was true when the other two matrix solutions were used. This perhaps shows the importance of Ca^{2+} ions in increasing P adsorption by soils and supports the previous report that Ca on the exchange sites increases P adsorption by soils (Helyar et al., 1976b; Smillie et al., 1987; Curtin et al., 1987).

Expressed as a percentage of total metal exchangeable with NH_4^+, the amount of alkali metal released from alkali metal-saturated soils during equilibrating soils with P made in different matrix solutions is shown in Table 18. Results showed that the amount of metal released was the least when water was the matrix solution and the greatest when 0.01 M $CaCl_2$ was the matrix solution. The amount of metal released when water was the matrix solution also increased with the increase in P addition. This can be attributed to the increase in the amount of K^+ introduced with the increase in P addition because KH_2PO_4 was used as a source of P. Although the greatest amount of metal ions released to the equilibrium solution was when $CaCl_2$ was used as a matrix solution, the amount of P adsorbed by soils was the greatest from this matrix solution. Thus, the increase in the amount of Ca^{2+} on the exchange sites, by replacing the monovalent alkali-metal cation saturating the exchange sites, largely increased P adsorption by soils. Other

Table 18. Effect of matrix solutions used in constructing phosphate adsorption isotherms on the release of exchangeable metals from alkali metal-saturated soils

Soil	Alkali metal	Percentage of metal released to equilibrium solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
		----------%[b]----------		
Hayden	Li	30.0-77.5	95.0-120	105-126
	Na	26.2-52.3	104-108	97-102
	K	24.5-55.5	ND[c]	72.7-96.4
	Rb	20.8-37.5	51.8-54.1	81.7-83.3
	Cs	19.3-41.5	100-113	87.9-97.8
Luther	Li	40.9-63.8	104-115	119-130
	Na	25.4-54.2	85.9-93.7	93.1-97.7
	K	26.0-55.3	ND	83.7-91.1
	Rb	16.1-32.1	48.1-51.3	73.8-73.8
	Cs	6.33-27.2	72.8-77.5	64.4-78.4
Lester	Li	35.7-62.8	88.4-93.8	92.2-115
	Na	27.4-50.5	78.0-83.3	94.1-98.9
	K	24.9-47.5	ND	91.7-126
	Rb	24.5-36.8	52.3-55.1	69.3-73.7
	Cs	10.2-30.3	65.3-72.8	72.1-76.9
Clarion	Li	25.3-60.4	101-106	118-131
	Na	21.2-38.1	75.0-77.5	84.3-90.7
	K	21.3-38.9	ND	91.0-84.4
	Rb	14.2-21.6	35.4-37.2	56.7-57.1
	Cs	12.0-24.3	61.9-72.5	72.0-81.5
Nicollet	Li	25.5-58.4	80.4-102	117-130
	Na	36.3-47.8	80.1-90.0	88.0-95.6
	K	20.6-39.9	ND	79.4-89.9
	Cs	8.5-21.6	55.4-66.0	60.2-68.8

[a]Metal released upon equilibration of soil with a range of phosphate concentrations made either in deionized H_2O, 0.01 M KCl, or in 0.01 M $CaCl_2$ (soil:solution ratio = 1.25). For individual values, see Appendix Tables 32-36.

[b]Percentage of total exchangeable metal as determined by extraction with neutral, 1 M NH_4OAc (for procedure, see footnote b of Table 17).

[c]Not determined.

investigators (Ellis and Truog, 1955) have found that P adsorption by clay minerals (e.g., montmorillonite) increased with increase in the percentage of saturation with Ca^{2+} ions and attributed this increase to the calcium phosphate complexes formed. However, it is difficult to separate the role of Ca^{2+} on the exchange sites from its role when in solution because work by Helyar et al. (1976a) showed that Ca^{2+} in solution rather than Ca^{2+} on the exchange sites plays a major role in P adsorption by soils.

Langmuir adsorption isotherms resulting from the data of the P adsorption by Hayden and Clarion soils are shown in Figures 24 and 25, respectively. Similar plots were obtained for P adsorption by the other three soils examined. Plotting the data according to the Langmuir equation was effective in linearizing the data (linear regression analysis with $r \geq 0.957^{**}$; significant at $\underline{P} < 0.01$) and further illustrating the variations in P adsorption among soils, treatments, and matrix solutions. The resulting values of X_m and k as affected by the matrix solutions are presented in Table 19. These values of X_m and k varied with soil, saturating cation, and the matrix solution. Values of k, in general, were the greatest when $CaCl_2$ was the matrix solution and the least when H_2O was the matrix solution. However, the X_m values showed a deviation from the general observation for k values. The same soil showed different X_m values depending on the matrix solution regardless of the saturating metal. In general, the X_m values were more

Figure 24. Langmuir isotherms for phosphate adsorption by Li-, Na-, K-, Rb-, or Cs-saturated Hayden soil as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and $(C)^2$ is the P concentration in the equilibrium solution

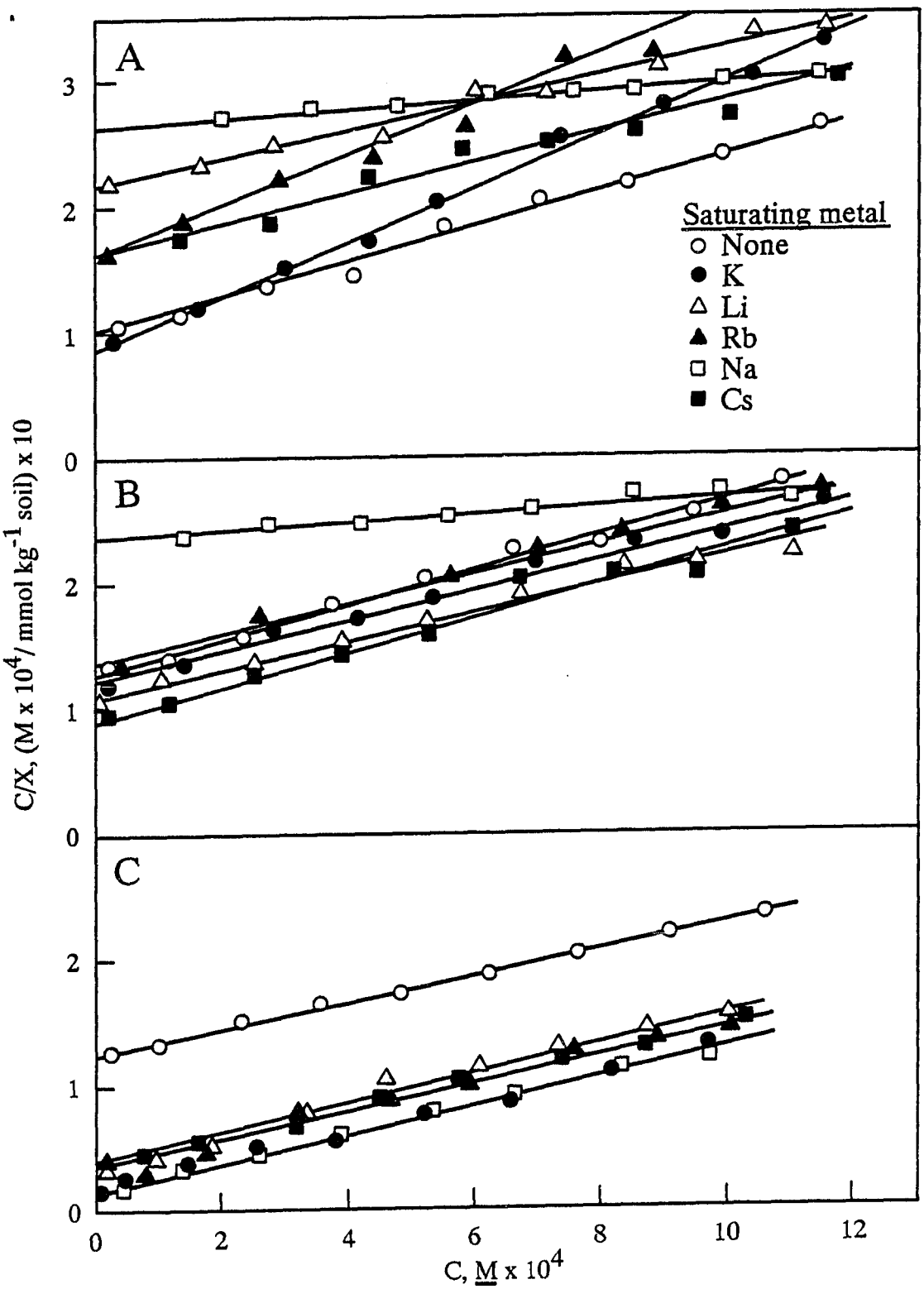

A
B
C
Saturating metal
None
K
Li
Rb
Na
Cs
C/X, (M x 10^4 / mmol kg^-1 soil) x 10
C, M x 10^4
0
1
2
3
4
6
8
10
12

Figure 25. Langmuir isotherms for phosphate adsorption by Li-, Na-, K-, Rb-, or Cs-saturated Clarion soil as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and $(C)^2$ is the P concentration in the equilibrium solution

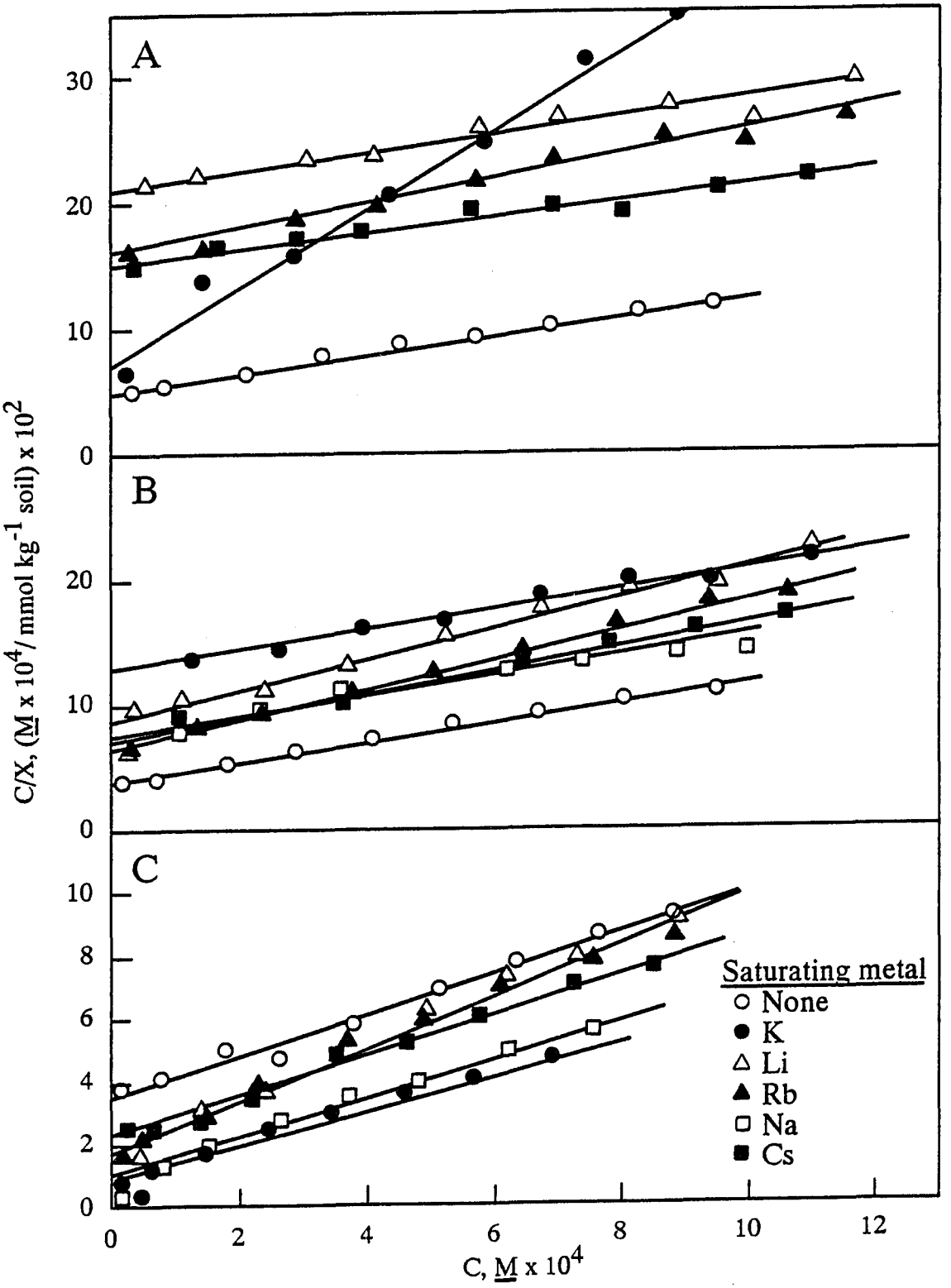

A
B
C
C/X, (M x 10^4/ mmol kg^-1 soil) x 10^2
C, M x 10^4
Saturating metal
None
K
Li
Rb
Na
Cs

Table 19. Langmuir constants for phosphate adsorption by alkali metal-saturated soils as affected by the equilibrium matrix solutions

Soil	Alkali metal	Water[a]		0.01 M KCl		0.01 M $CaCl_2$	
		X_m	k	X_m	k	X_m	k
Hayden	None[b]	6.77	1.52	7.41	1.71	9.71	1.39
	Li	8.87	0.53	8.41	1.17	8.31	3.25
	Na	33.2	0.11	24.2	1.01	8.50	9.50
	K	5.02	2.10	8.58	0.90	8.95	8.59
	Rb	5.00	1.27	7.42	1.08	8.22	3.81
	Cs	8.50	0.73	7.76	1.36	7.50	5.33
Luther	None	7.24	1.35	8.18	1.45	8.83	2.14
	Li	13.1	0.32	6.35	1.77	8.58	4.02
	Na	5.24	0.38	4.98	1.31	9.54	9.54
	K	6.47	1.00	12.0	0.43	10.3	8.87
	Rb	7.73	0.71	6.78	1.27	8.51	3.36
	Cs	6.42	0.97	5.12	3.75	8.96	3.99
Lester	None	6.19	1.76	6.08	2.45	8.57	3.07
	Li	10.2	0.51	9.19	0.62	9.18	4.36
	Na	2.33	0.45	15.0	0.20	9.42	6.64
	K	3.13	1.89	4.83	0.90	10.1	7.66
	Rb	5.59	1.04	5.29	1.87	8.29	4.82
	Cs	10.8	0.40	7.10	1.04	9.46	3.11
Clarion	None	14.1	1.00	12.9	2.15	16.2	1.00
	Li	15.2	0.31	8.53	1.27	11.1	6.42
	Na	6.10	0.31	13.7	0.96	14.7	9.71
	K	3.23	4.19	12.0	0.66	16.5	8.65
	Rb	10.1	0.63	8.36	1.81	12.3	4.50
	Cs	16.0	0.42	10.4	1.33	14.8	3.23
Nicollet	None	7.07	1.86	7.23	2.13	10.0	2.56
	Li	7.06	0.75	7.86	1.00	12.8	2.37
	Na	--	--	--	--	13.9	5.52
	K	6.31	0.94	9.55	0.57	13.9	6.01
	Cs	5.54	1.47	7.13	2.46	10.5	3.95

[a] X_m, adsorption maximum (mmol P kg^{-1} soil); k, affinity coefficient (reciprocal mmol L^{-1}) calculated from regression equations. (-) Indicates that the constants could not be calculated because the data did not fit the equation. All correlation coefficient values were >0.957 and were significant at $P>0.01$.

[b] None, natural (untreated) soil.

uniform when $CaCl_2$ was used as a matrix solution than when water or KCl was used as a matrix solution. The X_m values for Li- and Cs-saturated soils were the greatest in water matrix solution, whereas those for Na-, K-, and Rb-saturated soils were the greatest in $CaCl_2$ matrix solution.

The X_m and k values obtained in one matrix solution for different soils were also largely varied, i.e., no general trend could be found (Table 19). The X_m value was the greatest for Na-saturated Hayden soil when water or 0.01 M KCl was the matrix solution, whereas the greatest X_m value for the same soil was obtained with the untreated sample by using 0.01 M $CaCl_2$ as a matrix solution. For Lester and Clarion soils, the X_m values exhibited the same trend in water matrix solution: Cs > Li > untreated > Rb > K > Na. However, X_m values for these two soils exhibited different trends in the other two matrix solutions, and the greatest X_m values were obtained for Na-saturated and for K-saturated samples of both soils when 0.01 M KCl or 0.01 M $CaCl_2$ was used as a matrix solution, respectively. In fact, when $CaCl_2$ was the matrix solution, the greatest X_m values were observed for K-saturated soils.

Because the soil samples saturated with different alkali metals also exhibited differences in pH values (Table 20), it was recognized that the effect of alkali metal saturation on P adsorption, as discussed above, was to some extent confounded with the effect of pH. Although the pH of alkali metal-saturated soils (Table 20) was the greatest in water and the least in $CaCl_2$, maximum adsorption, whether inferred from isotherms or calculated according to the Langmuir equation, did not show

Table 20. pH values of alkali metal-saturated soils as measured in various aqueous solutions

Soil	Alkali metal	pH of soil in aqueous solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
Hayden	None[b]	5.50	5.26	4.97
	Li	6.86	5.80	5.10
	Na	8.54	7.78	6.60
	K	8.03	7.54	6.57
	Rb	6.48	6.00	5.15
	Cs	6.30	6.03	5.14
Luther	None	5.92	5.73	5.46
	Li	7.28	6.26	5.45
	Na	8.50	7.72	6.64
	K	8.10	7.64	6.58
	Rb	6.91	6.38	5.45
	Cs	6.92	6.44	5.42
Lester	None	6.50	6.39	6.10
	Li	7.94	7.22	6.02
	Na	8.72	8.12	6.72
	K	8.33	7.94	6.58
	Rb	7.59	7.15	6.11
	Cs	7.86	7.22	6.06
Clarion	None	5.80	5.70	5.36
	Li	7.35	6.50	5.34
	Na	8.54	7.89	6.56
	K	8.25	7.85	6.56
	Rb	7.03	6.49	5.34
	Cs	6.96	6.48	5.33
Nicollet	None	6.03	5.84	5.52
	Li	7.30	6.50	5.50
	Na	8.57	7.90	6.72
	K	8.21	7.80	6.56
	Cs	7.14	6.64	5.46

[a] Soil:H_2O, 0.01 M KCl or $CaCl_2$ ratio = 1:25.

[b] None, natural (untreated) soil.

the same trend (Figures 19-23, Table 19). Moreover, the k values were the least with the greatest pH, suggesting that the affinity of phosphate to the adsorption sites decreased with an increase in OH^- concentration. As discussed previously, this supports the conclusion that pH affects P adsorption through affecting other factors important in P adsorption (Barrow, 1984). The greatest pH was observed in the water suspension of Na- and K-saturated soils. However, with a few exceptions, P adsorption was the least for most soils saturated with either Na or K when water was the matrix solution as compared when KCl or $CaCl_2$ was the matrix solution. This seems to be contrary to the finding reported in Part II showing that P adsorption increased with increasing pH beyond the zero point of charge. But the low X_m values found for Na- and K-saturated soils could be due to secondary factors resulting from the relatively high pH values associated with soils when saturated with these metals. These secondary factors range from possible hydrolysis of native organic P resulting in competition with the added inorganic P to change in ionic strength of the equilibration solution.

PART V. EFFECTS OF EXCHANGEABLE ALKALINE EARTH METALS ON PHOSPHATE ADSORPTION BY SOILS

INTRODUCTION

Numerous studies have shown that clays retained more phosphate when Ca saturated than when H saturated (Allison, 1943; Chandler, 1941; Ragland and Seay, 1957; Wild, 1953). The hypothesis that phosphate can be adsorbed by clay through the intermediary of exchangeable Ca ions has been proposed as early as 1930 by Delmon and Barbier (as cited by Wild, 1953), because they observed that a soil-clay adsorbed less phosphate when acid saturated than when base saturated. Saturating kaolinite, montmorillonite, and Rothamested clay at pH 5.5 with different cations, Wild (1953) found that the retention of phosphate in the presence of Ca ions was more than in the presence of Na ions. Moreover, it has been reported that saturation of kaolinite, montmorillonite, and illite with divalent cations increased phosphate adsorption more than saturation with monovalent cations or without saturation (Pissarides et al., 1968).

Other reports indicate that exchangeable cations may affect the amount of phosphate released by soils in a way that the release of P from monovalent cation-saturated soils exceeded that of divalent cation-dominated soils (Barrow, 1984; Curtin et al., 1987; Smillie et al., 1987).

Most of the previous studies on the effect of alkaline earth metals on phosphate adsorption have been done with clay minerals. Little information is available on the effect of saturating the exchange sites of soils on phosphate adsorption isotherms. Work reported in Part IV

showed that saturating soils with alkali metal markedly affected phosphate adsorption by soils, and this effect was related to the type of matrix solution used. In this part, the effect of the alkaline earth metals on phosphate adsorption is reported. The soils were converted to monoionic forms by using Mg, Ca, Sr, and Ba; and the phosphate adsorption by these soils was studied. An additional objective was to assess the effect of matrix solution on phosphate adsorption by the alkaline earth metal-saturated soils.

DESCRIPTION OF METHODS

Soils

The soils used in this study were Hayden, Luther, Lester, Clarion, and Nicollet. These soils were chosen because of their similarity in pH and because they gave a range in soil organic matter and cation-exchange capacity. The pertinent properties of these soils are reported in Table 1, Materials and Methods section.

The soils were converted to monoionic forms by saturating the exchange sites with each of the alkaline earth metals (Mg, Ca, Sr, or Ba). The monoionic soil forms were prepared by the same procedures used in Part II for preparing NH_4-saturated soils. These procedures can be summarized as follows: neutral, 0.5 M solution of either acetate or chloride salt of each metal (Table 21) was used to saturate the negative sites of the soils. After filtration, the excess solution was leached out by 0.125 M chloride salt of the saturating metal. Isopropyl alcohol was used to remove the free salt solution. Before use, all metal solutions were adjusted to pH 7 by 0.1 M of either HCl or KOH (Table 21). Salts of all alkaline earth metals used in this part of the study were in the acetate form, except Sr which was in the chloride form. With the exception of Mg acetate which was a Baker-analyzed reagent (J. J. Baker Chemical Co., Phillipsburg, NJ), all metal salts were Fisher certified reagents (Fisher Scientific Co., Itasca, IL).

Table 21. Alkaline earth metal salts used in converting soils to monoionic forms

Alkaline earth metal	Alkaline earth metal salt used	Formula weight	Concentration[a] M	pH[b]
Mg	$Mg(CH_3COO)_2.4H_2O$	214.5	0.5	8.15
Ca	$Ca(CH_3COO)_2$	176.2	0.5	8.37
Sr	$SrCl_2.6H_2O$	266.6	0.5	5.64
Ba	$Ba(CH_3COO)_2$	255.4	0.5	8.46

[a]Prepared in deionized water.

[b]One half of the formula weight was dissolved in about 600 mL of deionized water and the solution was titrated to pH 7.0 with 0.01 M HCl or KOH before adjusting the volume to 1 L.

The pH (soils:solution ratio, 1:25) of the alkaline earth metal-saturated soils was determined in water, 0.01 M KCl, and 0.01 M $CaCl_2$ by using a glass electrode.

The exchangeable alkaline earth metals of the metal-saturated soils were extracted with neutral, 1 M NH_4OAc and determined as described in Part IV.

Reagents

Stock solutions

The stock solutions needed for this study were prepared as described in Part III. These were 32.3 mM KH_2PO_4, 1 M $CaCl_2$, and 1 M KCl.

Phosphate-working solutions

The 10 standard working solutions used in Part III were used in this study. These standard solutions were made in water, 0.01 M KCl, or 0.01 M $CaCl_2$ as described in Part III.

Determination of the phosphate adsorption isotherms

Phosphate adsorption isotherms for the alkaline earth metal-saturated soils, as affected by the matrix solutions, were constructed as described in Part III for the effect of pH on phosphate adsorption.

Alkaline earth metals released from the metal-saturated soils to the matrix solution during equilibration of soil with the range of P concentrations, used to construct the adsorption isotherms, were determined in the clear filtrate obtained to determine the P remaining in the equilibrium solution. All metals were determined by atomic absorption spectrophotometry (Perkin-Elmer Model 5000).

RESULTS AND DISCUSSION

The effect of saturating the exchange sites with alkaline earth metal on phosphate adsorption from water, 0.01 M KCl, or 0.01 M $CaCl_2$ solution by Hayden, Luther, Lester, Clarion, and Nicollet soils is shown in Figures 26-30, respectively. As indicated by the shapes and locations of the adsorption isotherms, the amount of P adsorbed increased with increase of P in the equilibrium solution. However, all the isotherms showed a diminishing rate of increase in the amount of P adsorbed with increasing equilibration concentration. The isotherms also showed a very steep slope at the start (i.e., at low initial P concentration) which can be attributed to a high affinity for adsorption of P by soils after saturation with alkaline earth metals. In general, all adsorption isotherms were characterized by a marked inflection point which appears to be dependent on the saturating metal, soil type, and to a lesser extent on the type of matrix solution. However, none of the isotherms exhibited a real saturation zone, which is normally associated with a relatively long plateau of minimum slope immediately after the inflection point. On the contrary, a continuous though gradual increase in P adsorption with increase in initial P concentration addition was the most common among all isotherms.

Giles et al. (1960) reviewed the literature on classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. They

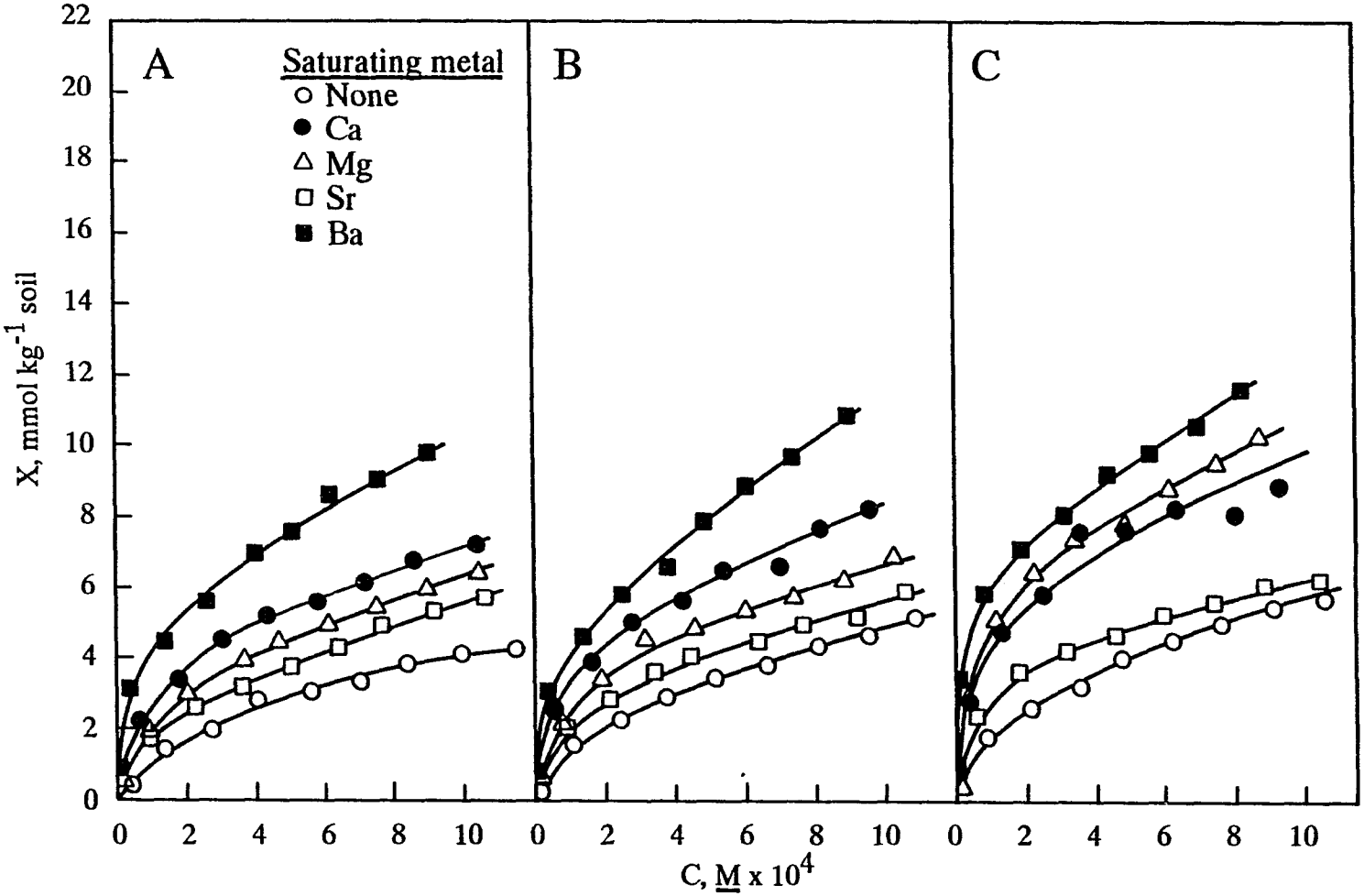


Figure 26. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Hayden soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

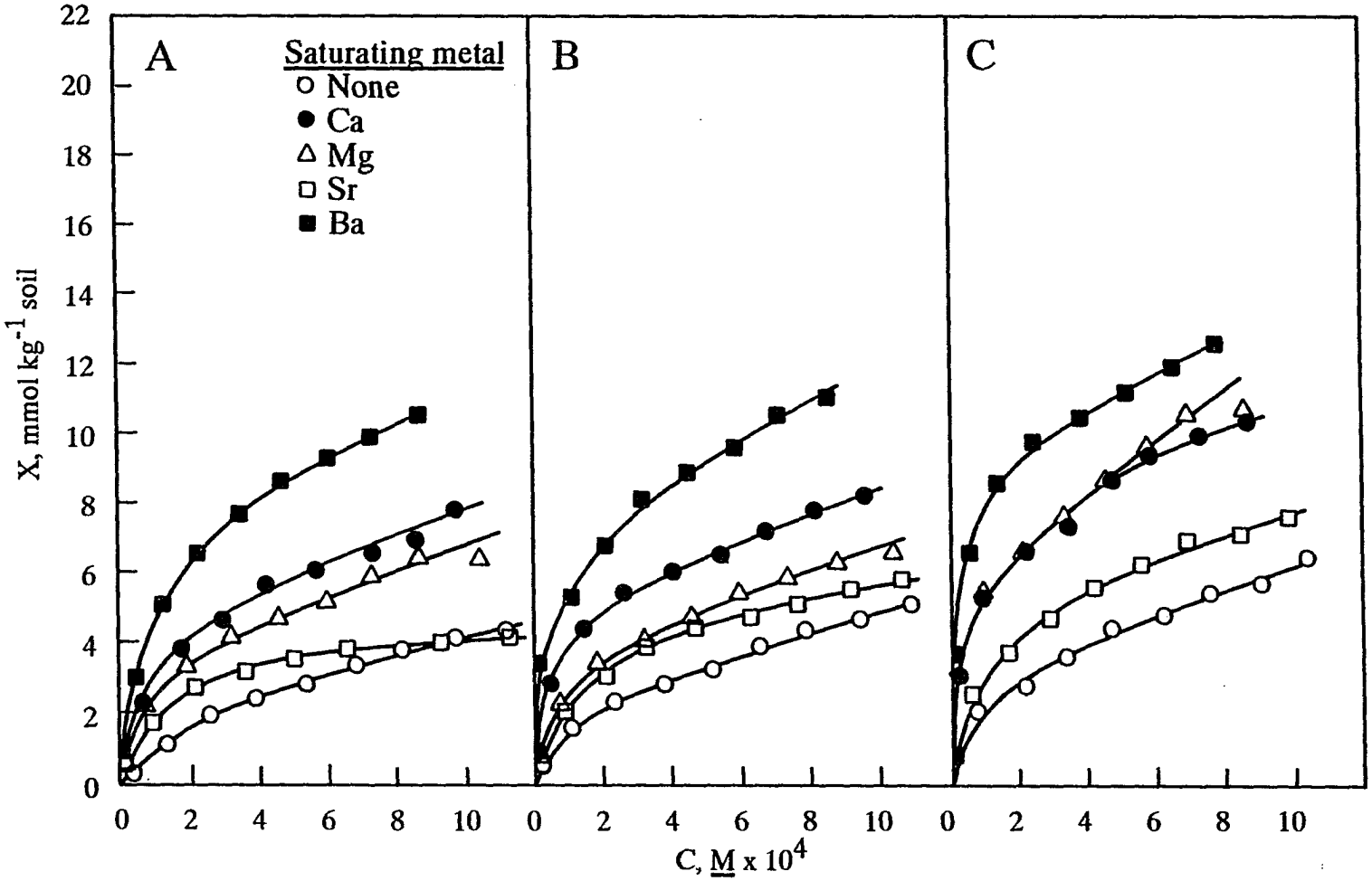


Figure 27. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Luther soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

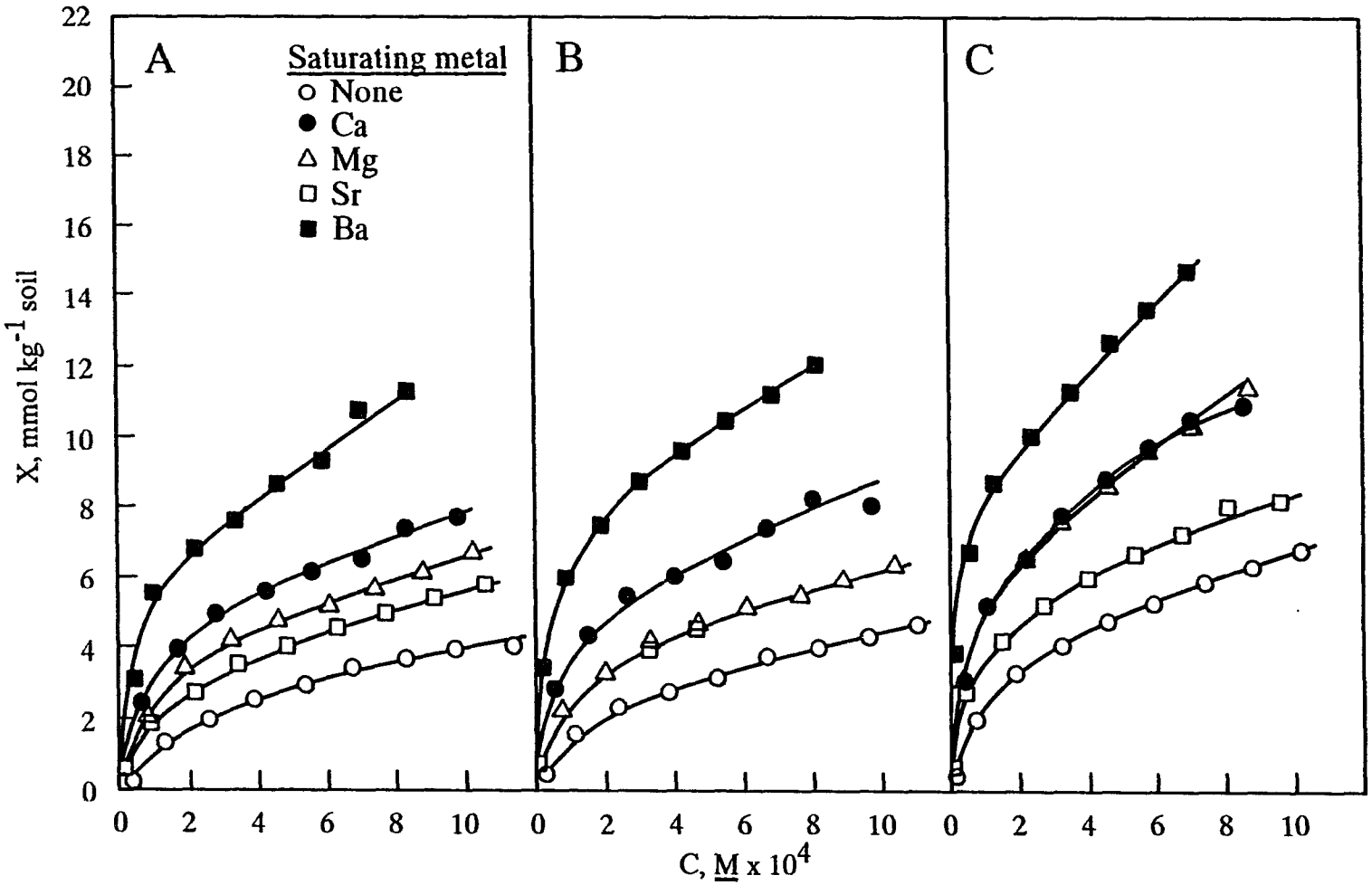


Figure 28. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Lester soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

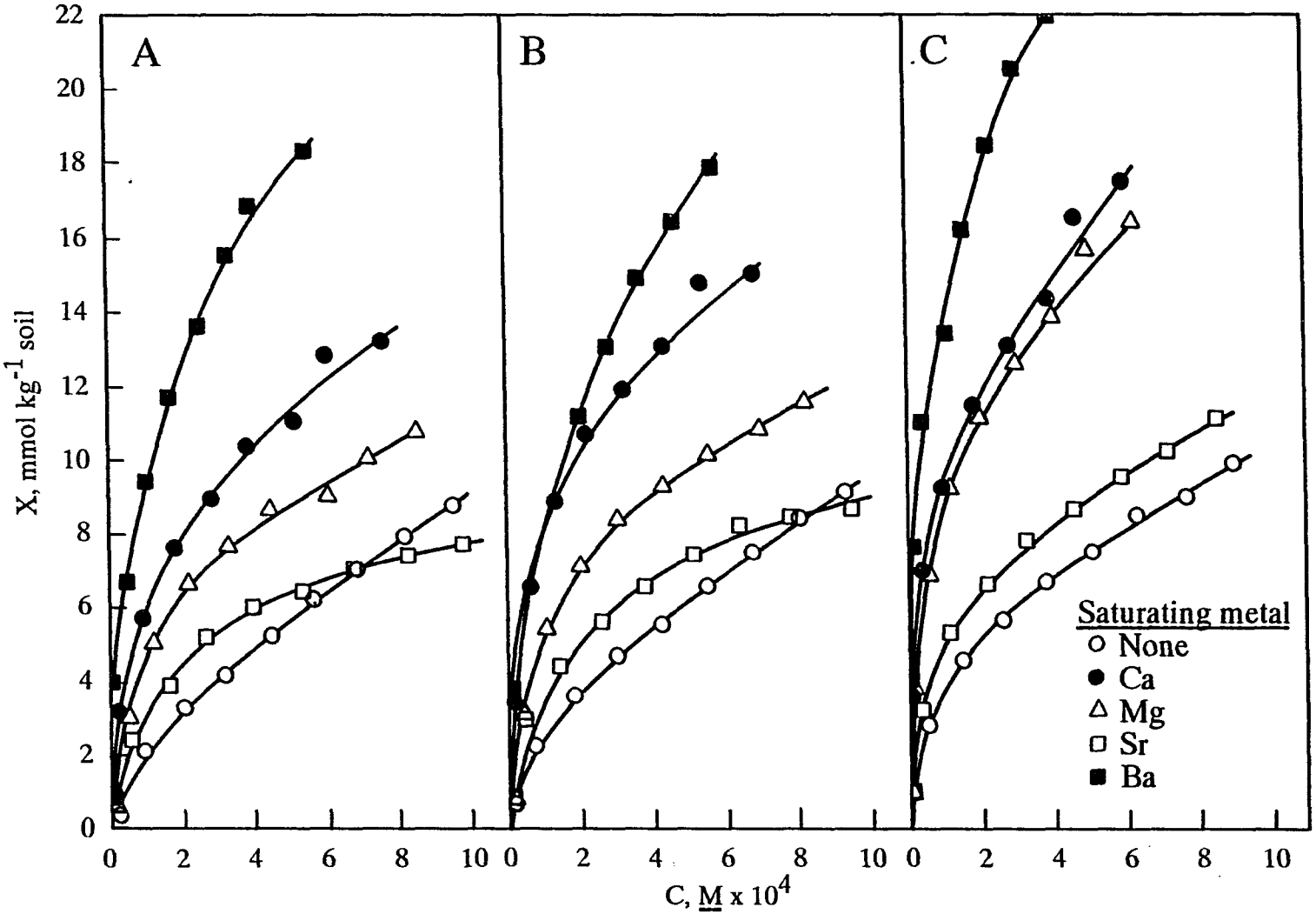


Figure 29. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Clarion soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

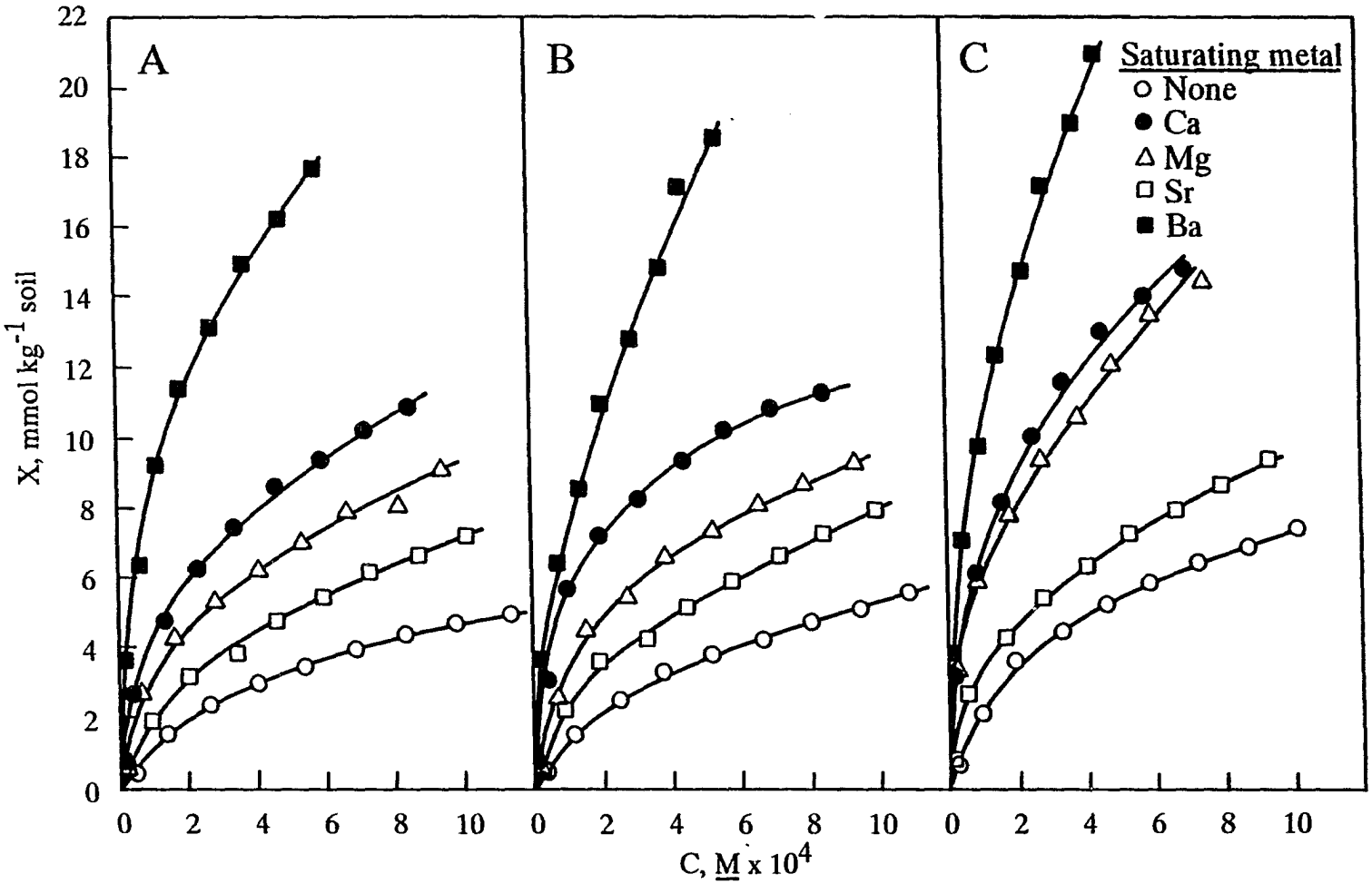


Figure 30. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Nicollet soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

showed that the present system divides all isotherms into four main classes according to the initial slope, and subgroups can be described for each class based on the shape of the upper parts of the curves. The four main classes are named the S, L (i.e., "Langmuir" type), H ("high affinity"), and C ("constant partition") isotherms. Phosphate adsorption isotherms in the three matrix solutions used in this study can be categorized into L type for Hayden, Luther, and Lester soils and into H type for alkaline earth metal-saturated Clarion and Nicollet soils. The L curves which represent Langmuir type isotherms are the best known type of isotherm. In fact, the L type exhibited an inflection point which shows that as more adsorbing sites are filled it becomes increasingly difficult for phosphate ions in solution to find a vacant adsorbing site available. On the other hand, the H type of curve is a special case of the L curve in which the P has such high affinity that in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in solution. The initial part of the isotherm is therefore almost vertical, which is the case for Clarion and Nicollet soils saturated with alkaline earth metals.

The amount of P adsorbed by soils saturated with an alkaline earth metal at any given equilibrium solution was much higher than the amount adsorbed by the same soils but saturated with alkali metals (reported in Part IV). This observed higher amount of P adsorption by soils saturated with divalent alkaline earth metals than with alkali metal supports the conclusions reached by Pissarides et al. (1968) who showed

high P adsorption by clay minerals saturated with one of either alkali (Li, Na, and K) or alkaline earth metals (Mg, Ca, Sr, and Ba). They explained this finding as follows: according to Wiklander (1964) the thickness of the diffuse double layers are inversely proportional to the valency of the saturating cations. Wiklander also reported that Donnan theory predicts that the activity of the phosphate ion in the vicinity of the clay particles should increase as the valency of saturating cation increases. Therefore, the accessibility of the clay surface to phosphate in the adsorption reaction should be greater with divalent cations than with monovalent cations on the exchange complex. The greater P adsorption by soils saturated with divalent cations than that of the same soils but saturated with monovalent cations in different matrix solutions is in agreement with the findings of Pissarides et al. (1968), Ragland and Seay (1957), and Wild (1953) who reported more P adsorption by clay minerals saturated with divalent cations than with monovalent cations.

The effect of matrix solutions on the amount of P adsorbed by soil at any given P concentration is less pronounced than that of the same soil saturated with alkali metals (see Part IV). This may be attributed to the fact that ionic composition of equilibrating solution will affect the extent of ion exchange between soil particles and the equilibration solution. Consequently, some of the ions on exchange sites of soils will come into the solution upon equilibration. Potassium and Ca^{+} ions are the replacing ions when KCl and $CaCl_2$ were matrix solutions,

respectively. Table 22 shows the effect of matrix solutions on the release of exchangeable metals from alkaline earth metal-saturated soils. The greatest amount of metal released was when $CaCl_2$ was the matrix solution. However, the release of metal ions from the saturating sites varied with the four alkaline earth metals studied. In general, the least amounts were released from Ba-saturated soils (49.9-56.2%), followed by Sr-saturated soils (58.0-91.4%), followed by Mg-saturated soils (77.3-94.0%). The least amounts of metal released were found when water was used as a matrix solution. In general, the percentage of exchangeable Mg, Ca, Sr, and Ba released to the matrix solution varied with soil, alkaline earth metal used, and matrix solution employed.

Although the effect of matrix solution on P adsorption by alkaline earth metal-saturated soils was not as great as that on P adsorption by alkali metal-saturated soils (compare Figures 19-23 with Figures 26-30), the amount of P adsorbed varied with matrix solution in the following order: $CaCl_2$ > KCl > water. Moreover, in the three matrix solutions, the alkaline earth metal-saturated soils exhibited a general trend of P adsorption as follows: Ba-saturated soils > Ca-saturated > Mg-saturated > Sr-saturated > untreated soils. This sequence of P adsorption as affected by the saturating metals is in the same order as the amounts of these metals on the exchange sites (Table 23). Obviously, the CEC values obtained by using Mg^{2+}, Ca^{2+}, and Ba^{2+} as saturating ions were much higher than the CEC values as determined by the conventional ammonium acetate method. In fact, the CEC of the soils

Table 22. Effect of matrix solutions used in constructing phosphate adsorption isotherms on the release of exchangeable metals from alkaline earth metal-saturated soils

Soil	Alkaline earth metal	Percentage of metal released to equilibrium solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
		----------%[b]----------		
Hayden	Mg	22.4-34.3	58.2-64.2	83.6-94.0
	Ca	19.1-23.6	50.5-57.2	ND[c]
	Sr	12.1-16.5	50.6-56.7	65.4-91.4
	Ba	12.5-15.7	25.0-31.2	50.0-56.2
Luther	Mg	14.8-25.0	44.3-47.7	77.3-83.0
	Ca	14.8-21.1	48.5-52.7	ND
	Sr	8.3-14.1	34.8-38.4	67.8-74.7
	Ba	10.0-12.5	27.5-30.0	75.0-80.0
Lester	Mg	23.0-34.0	42.0-46.0	78.2-85.0
	Ca	14.0-18.7	40.0-44.0	ND
	Sr	8.9-12.0	22.4-24.6	69.2-66.6
	Ba	10.7-12.5	19.6-23.1	49.9-53.4
Clarion	Mg	15.7-20.9	32.7-35.9	79.1-82.4
	Ca	14.5-20.1	48.6-52.0	ND
	Sr	12.0-14.9	27.1-30.2	65.1-71.4
	Ba	12.5-14.1	21.9-25.0	50.0-56.2
Nicollet	Mg	17.8-22.4	37.5-42.1	79.6-81.6
	Ca	14.3-16.3	38.1-42.4	ND
	Sr	13.0-16.4	28.2-30.9	58.0-61.5
	Ba	21.9-25.0	21.9-26.6	49.9-53.4

[a]Metal released upon equilibration of soil with a range of phosphate concentrations made either in deionized H_2O, 0.01 M KCl, or 0.01 M $CaCl_2$ (soil:solution ratio = 1:25). For individual values, see Appendix Tables 37-40.

[b]Percentage of total exchangeable metal as determined by extraction with neutral, 1 M NH_4OAc (for procedure, see footnote b of Table 17).

[c]Not determined.

Table 23. Cation-exchange capacity of soils as determined by using NH_4OAc or alkaline earth metal salt solutions

Saturation ion[b]	CEC of soil indicated[a]				
	Hayden	Luther	Lester	Clarion	Nicollet
	cmol (+) kg^{-1} soil				
NH_4^+	10.5(100)	14.0(100)	19.5(100)	25.9(100)	25.8(100)
Mg^{2+}	12.9(123)	16.9(121)	26.0(133)	30.0(116)	29.8(116)
Ca^{2+}	17.8(170)	18.9(135)	30.0(154)	35.8(138)	36.7(142)
Sr^{2+}	10.8(103)	15.2(109)	24.6(126)	28.0(108)	28.4(110)
Ba^{2+}	17.1(163)	21.4(153)	30.0(154)	34.2(132)	34.2(133)

[a]Figures in parentheses are CEC values expressed as percentages of the values obtained by using neutral, 1 M NH_4OAc.

[b]For methods and procedures, see footnote b of Table 17, Part IV.

as determined by the amount of metal retained on the exchange sites was in the following order: $Ca^{2+} > Ba^{2+} > Mg^{2+} > Sr^{2+} > NH_4^+$. Thus, with the exception of Ca^{2+} and Ba^{2+} which changed position in the sequence P adsorption by alkaline earth metal-saturated soils, P adsorption by the metal-saturated soils followed the sequence of CEC values as determined by using different alkaline earth metals.

The other possible reason which may explain the aforementioned trend of P adsorption by alkaline earth metal-saturated soils as affected by the matrix solutions is the pH of the metal-saturated soils. Although samples of soils saturated with different cations should

exhibit differences in pH values, pH values of Mg-, Ca-, and Ba-saturated soils as determined in water, 0.01 M KCl, or 0.01 M $CaCl_2$ matrix solution were similar (Table 24). The pH values of untreated and Sr-saturated samples of soils are, however, relatively similar but lower than those of either Mg^{2+}-, Ca^{2+}-, or Ba^{2+}-saturated soil samples. Thus, the larger amounts of P adsorption by the soil samples with higher pH than with lower pH (Figures 26-30, Table 24) support the conclusion made in Part II concerning the effect of pH on P adsorption. However, the differences in the amounts of P adsorbed by soils saturated with different alkaline earth metals (i.e., homoionic soils) could be attributed to the nature of the various cations as it was suggested by Chandler (1941) because the differences in pH values of soils saturated with Mg, Ca, or Ba is small and cannot account for the large differences found for P adsorption when soils were saturated by these metals.

As it was discussed in Part II, the Langmuir equation is used to summarize the many results of adsorption isotherms. The reasoning for using this model over the other models was also given in Part II. The Langmuir adsorption isotherms resulting from the P adsorption by alkaline earth metal-saturated Hayden and Clarion soils as affected by matrix solutions are shown in Figures 31 and 32, respectively. Similar plots were obtained for adsorption of phosphate by the other three soils studied. These figures showed that plotting the data according to the Langmuir equation was effective in linearizing the data and further illustrating the variations in adsorption of P among soils and within

Table 24. pH values of alkaline earth metal-saturated soils as measured in various aqueous solutions

Soil	Alkaline earth metal	pH of soil in aqueous solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
Hayden	None[b]	5.50	5.26	4.97
	Mg	7.54	7.50	7.30
	Ca	7.50	7.44	7.18
	Sr	5.56	5.48	5.24
	Ba	7.16	7.16	6.90
Luther	None	5.92	5.73	5.46
	Mg	7.47	7.41	7.14
	Ca	7.47	7.33	7.14
	Sr	6.02	5.85	5.60
	Ba	7.20	7.15	6.88
Lester	None	6.50	6.39	6.10
	Mg	7.70	7.63	7.29
	Ca	7.57	7.54	7.27
	Sr	6.56	6.55	6.15
	Ba	7.38	7.35	7.01
Clarion	None	5.80	5.70	5.36
	Mg	7.38	7.39	7.08
	Ca	7.28	7.29	7.04
	Sr	5.81	5.80	5.42
	Ba	7.25	7.20	7.87
Nicollet	None	6.03	5.84	5.52
	Mg	7.50	7.43	7.13
	Ca	7.40	7.31	7.10
	Sr	6.00	5.98	5.62
	Ba	7.22	7.17	6.88

[a] Soil:H_2O, 0.01 M KCl or $CaCl_2$ ratio = 1:25.

[b] None, natural (untreated) soil.

Figure 31. Langmuir isotherms for phosphate adsorption by Hayden soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution

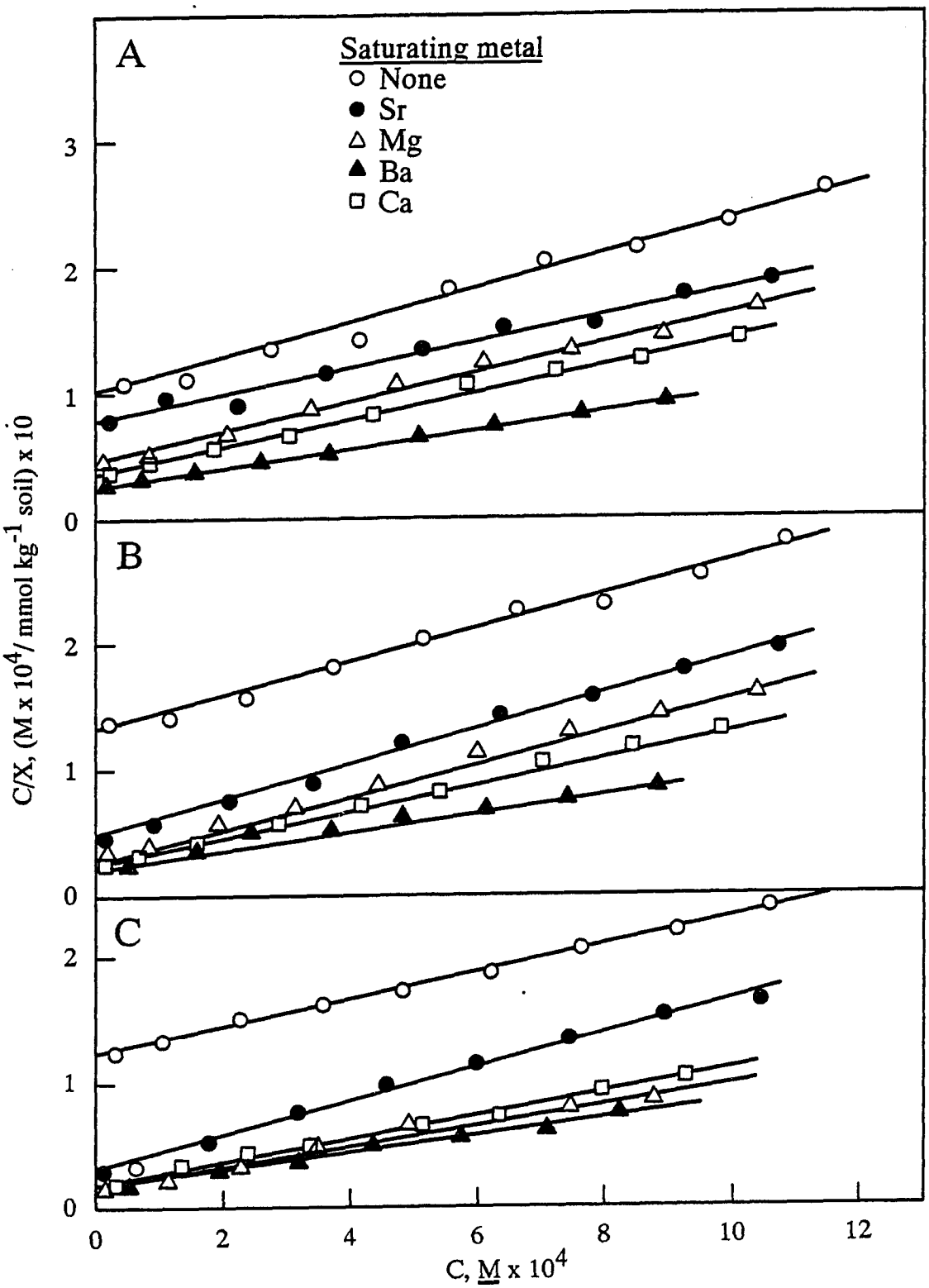
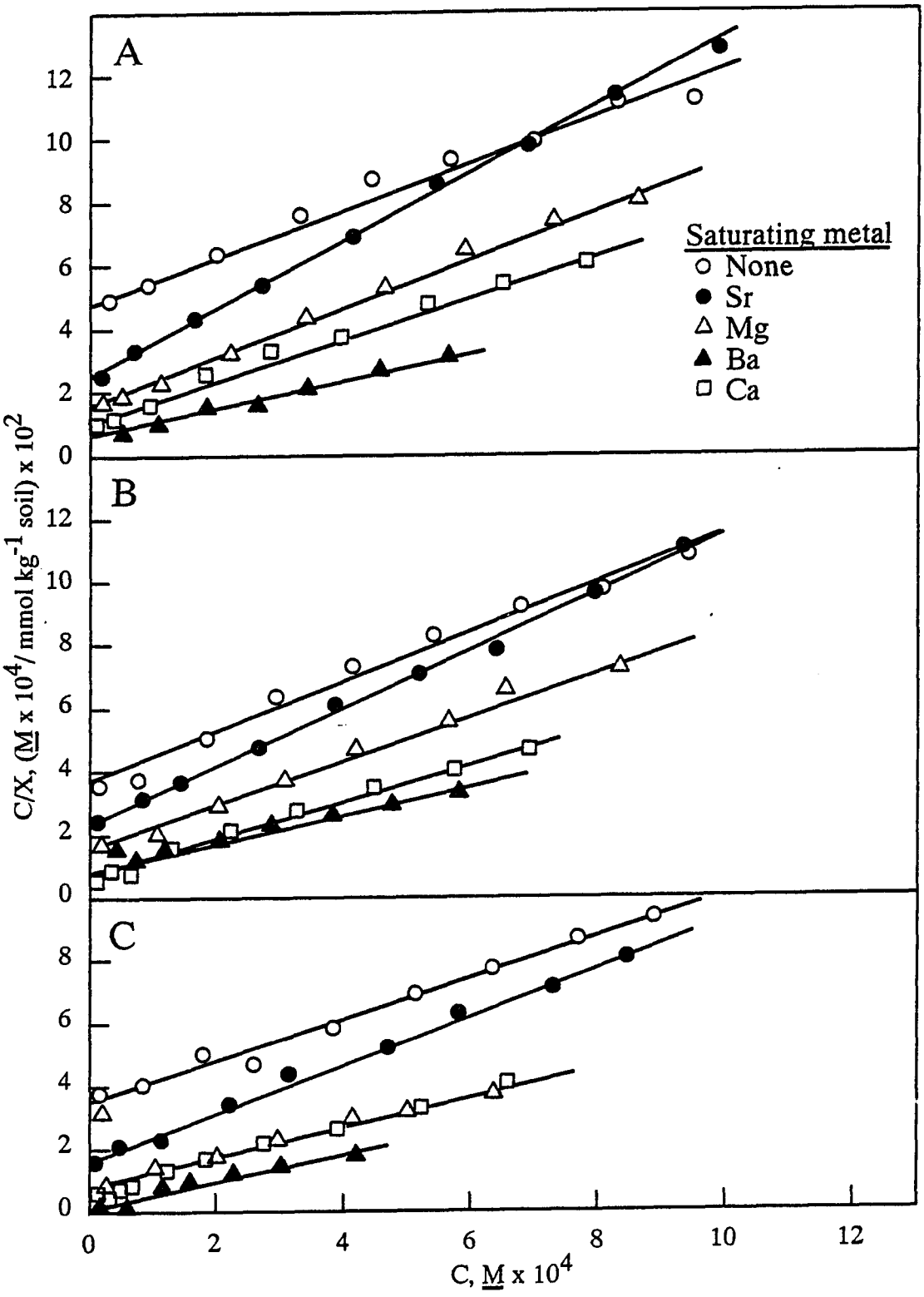

A
B
C
Saturating metal
None
Sr
Mg
Ba
Ca
C/X, (M x 10^4/ mmol kg^-1 soil) x 10
C, M x 10^4
0
1
2
3
4
6
8
10
12

Figure 32. Langmuir isotherms for phosphate adsorption by Clarion soil saturated with Mg, Ca, Sr, or Ba as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution


A
B
C
Saturating metal
None
Sr
Mg
Ba
Ca
C/X, (M x 10^4/ mmol kg^-1 soil) x 10^2
C, M x 10^4
0
2
4
6
8
10
12

alkaline earth metal-saturated samples of the same soils. The resulting values of the adsorption maximum (X_m) and the affinity coefficient (k) for the adsorption of P by soils saturated with alkaline earth metals are presented in Table 25. The effect of matrix solutions on P adsorption maxima for all samples of untreated (original) soils were in the following order: $CaCl_2$ > KCl > water. Moreover, samples of the soils saturated with either Ca^{2+}, Sr^{2+}, or Ba^{2+} exhibited the same trend of X_m values in the three matrix solutions, similar to that observed for the untreated soils. However, when Mg was the saturation metal, different soils exhibited a different trend of X_m values in different matrix solutions. In fact, Hayden, Luther, and Lester soils saturated with Mg^{2+} showed the following general trend of X_m values: $CaCl_2$ > water > KCl. On the other hand, X_m values were the greatest in water and $CaCl_2$ for Clarion and Nicollet soils, respectively. The least X_m values for both soils were obtained in $CaCl_2$ solution for Clarion soil and water for Nicollet soils.

The affinity coefficient values of untreated Luther, Lester, and Nicollet soils were the greatest in $CaCl_2$ and the least in water as a matrix solution. However, for Hayden and Clarion soils the greatest k values were found when KCl was the matrix solution and the least when $CaCl_2$ was the matrix solution. In general, the k values for alkaline earth metal-saturated samples of the soils as affected by the matrix solutions were in the following order: $CaCl_2$ > KCl > H_2O.

Table 25. Langmuir constants for phosphate adsorption by alkaline earth metal-saturated soils as affected by the equilibrium matrix solution

Soil	Alkaline earth metal	Water[a]		0.01 M KCl		0.01 M $CaCl_2$	
		X_m	k	X_m	k	X_m	k
Hayden	None[b]	6.77	1.52	7.41	1.71	9.71	1.39
	Mg	8.34	2.79	7.79	4.24	11.6	6.18
	Ca	9.40	2.88	9.24	4.21	10.1	7.08
	Sr	9.50	1.39	6.90	3.32	7.06	5.67
	Ba	13.8	2.69	13.1	3.47	14.5	1.03
Luther	None	7.24	1.35	8.18	1.45	8.83	2.14
	Mg	8.22	3.38	8.20	3.59	12.7	5.63
	Ca	8.30	5.24	9.62	5.20	12.3	5.82
	Sr	4.74	6.40	7.12	3.70	9.53	3.75
	Ba	13.1	4.51	13.5	4.93	13.1	15.1
Lester	None	6.19	1.76	6.08	2.45	8.57	3.07
	Mg	9.34	2.23	7.85	3.35	12.3	6.23
	Ca	8.47	5.14	9.48	5.03	13.9	4.24
	Sr	7.55	2.65	7.40	4.09	9.93	4.58
	Ba	12.6	5.28	13.6	6.79	16.0	8.94
Clarion	None	14.1	1.00	12.9	2.15	16.2	1.00
	Mg	26.7	2.88	13.9	5.15	12.7	4.91
	Ca	14.8	6.77	17.1	8.37	18.2	9.14
	Sr	9.49	4.39	11.1	3.93	13.5	4.37
	Ba	23.5	4.73	22.7	6.48	24.1	16.9
Nicollet	None	7.07	1.86	7.23	2.13	10.0	2.56
	Mg	9.88	4.59	11.9	3.36	16.2	6.20
	Ca	14.5	3.29	12.6	7.95	17.4	7.17
	Sr	13.1	1.22	13.8	1.34	13.7	2.29
	Ba	22.2	5.63	31.0	2.69	27.8	5.99

[a] X_m, adsorption maximum (mmol P kg^{-1} soil); k, affinity coefficient (reciprocal mmol L^{-1}) calculated from regression equations. All correlation coefficient values were >0.989 and were significant at $P < 0.01$.

[b] None, natural (untreated) soil.

Adsorption maxima values of a soil saturated with different alkaline earth metals equilibrated in the same matrix solution were different depending on the saturating metal. For example, when water was the matrix solution, the order of the X_m values with different saturating metals for all soils were as follows: Ba > Mg > Ca > Sr > untreated; whereas in the KCl matrix solution the order was: Ba > Ca > Mg > untreated $\geq$ Sr; and in $CaCl_2$ it was: Ba > Mg $\geq$ Ca > Sr > untreated.

The possibility of precipitation of the phosphate with the Ca, Mg, and Ba released to the matrix solution was considered but rejected because calculation of the solubility of phosphates of these elements showed that, at the pH values of the soil-phosphate-matrix solution, these phosphates are soluble and very unlikely resulted in precipitation. The possible formation of the insoluble $SrHPO_4$ was also considered but again rejected because the amounts of Sr released to the matrix solution were not affected by the increase in phosphate concentration and because the phosphate adsorption isotherms obtained for soils saturated with Sr were not different from those obtained for soils saturated with Mg, Ca, or Ba.

PART VI. EFFECTS OF EXCHANGEABLE HEAVY METALS ON PHOSPHATE ADSORPTION BY SOILS

INTRODUCTION

Extensive literature is available on the reaction behavior of heavy metals in soils (Adriano, 1986; Ellis and Knezek, 1972; Haque and Subramanian, 1982). These range from the plant availability to toxicity associated with these metals. Among the heavy metals, Mn, Cu, and Zn are considered essential elements for plant growth and development; whereas elements such as Cd, Ni, and Pb are considered toxic. The chemistry of these and other heavy metals in soils can qualitatively be described as affected by (1) the specific adsorption or exchange adsorption at given mineral surface, (2) the precipitation of sparingly soluble compounds of which they are constituent, and (3) the formation of relatively stable complex ions or chelates which result from the interaction with soil organic matter (Santillan-Medrano and Jurinak, 1975).

Studies on the reactions of phosphate with soluble and exchangeable Ni on clays by Pratt et al. (1964) demonstrated that Ni-saturated clays treated with phosphate showed the same reactions as found in solution. The exchangeable Ni was reduced to about 30%. Other studies by Nriagu (1972, 1973a,b) suggested that indigenous soil phosphate is an important buffering agent for Pb in the soil solution and, as a consequence, Pb phosphate formation can serve as a sink for P in ecosystems. A survey of the literature revealed little information on the effect of exchangeable heavy metals on phosphate adsorption.

Work reported in Parts IV and V showed that saturating soils with alkali and alkaline earth metals markedly affected phosphate adsorption by soils, and this effect was related to the type of matrix solution used. In this part, the effect of exchangeable heavy metals on phosphate adsorption is reported. The soils were converted to monoionic forms by using Mn, Ni, Cu, Zn, Cd, and Pb; and the phosphate adsorption by these soils was studied. An additional objective was to assess the effect of matrix solution on phosphate adsorption by the heavy metal-saturated soils.

DESCRIPTION OF METHODS

Soils

The soils used in this study were Hayden, Luther, Lester, Clarion, and Nicollet soils. These soils were chosen because of their similarity in pH and because they gave a range in soil organic matter content and cation-exchange capacity. The pertinent properties of these soils are reported in Table 1, Materials and Methods section.

The soils were converted to monoionic forms by saturating the exchange sites with each of the following heavy metals (Mn, Ni, Cu, Zn, Cd, or Pb). The monoionic soil forms were prepared by the same procedures used in Part II for preparing the NH_4-saturated soils. These procedures can be summarized as follows: 0.5 M solution of either acetate or chloride salts of each metal (Table 26) was used to saturate the negative sites of the soils. After filtration, the excess solution was leached out by 0.125 M chloride salt of the saturating metal. Isopropyl alcohol was used to remove the free salt solution. Before use, Mn and Ni solutions were adjusted to pH 7 by 0.1 M KOH (Table 26), but the solutions of the other metals were not adjusted because of precipitation problems. Salts of Cu, Zn, Ni, and Pb metals used in this study were in acetate form; whereas those of Mn and Cd were in chloride form. Salts of Mn, Cu, Cd, and Pb were Fisher certified reagents (Fisher Scientific Co., Itasca, IL); whereas the Ni salt was a Baker-analyzed reagent (J. J. Baker Chemical Co., Phillipsburg, NJ), and Zn was an analytical reagent (Mallinckrodt Inc., St. Louis, MO).

Table 26. Heavy metal salts used in converting soils to monoionic forms

Heavy metal	Heavy metal salt used	Formula weight	Concentration[a] M	pH
Mn	$MnCl_2.4H_2O$	197.9	0.5	3.60[b]
Ni	$Ni(CH_3COO)_2.4H_2O$	248.8	0.5	6.48[b]
Cu	$Cu(CH_3COO)_2.H_2O$	199.7	0.5	5.05[c]
Zn	$Zn(CH_3COO)_2.2H_2O$	219.5	0.5	6.08[c]
Cd	$CdCl_2.2.5H_2O$	228.3	0.5	5.05[c]
Pb	$Pb(CH_3COO)_2.3H_2O$	379.3	0.5	5.82[c]

[a]Prepared in deionized water.

[b]One half of the formula weight was dissolved in about 600 mL of deionized water and the solution was titrated to pH 7.0 with 0.01 M KOH before adjusting the volume to 1 L.

[c]pH was not adjusted due to precipitation.

The pH (soil:solution ratio, 1:25) of the heavy metal-saturated soil was determined in water, 0.01 M KCl, and 0.01 M $CaCl_2$ by using a glass electrode.

The exchangeable heavy metals of the metal-saturated soils were extracted with neutral, 1 M NH_4OAc and determined by atomic absorption spectrophotometry.

Reagents

Stock solutions

The stock solutions needed for this study were prepared as described in Part III. These were 32.3 mM KH_2PO_4, 1 M KCl, and 1 M $CaCl_2$.

Phosphate-working solutions

The 10 standard working solutions used in Part III were used in this study. The standard solutions (0 to 40 mg P L^{-1}) used for studies of phosphate adsorption by Mn-, Ni-, and Cd-saturated soils were made in water, 0.01 M KCl, or 0.01 M $CaCl_2$ as described in Part II. The phosphate concentrations in studies of phosphate adsorption by Zn-, Cu-, and Pb-saturated soils ranged from 0 to 140 mg P L^{-1}.

Determination of the phosphate adsorption isotherms

Phosphate adsorption isotherms for the heavy metal-saturated soils, as affected by the matrix solutions, were constructed by the same procedure described in Part III for the effect of pH on phosphate adsorption, but the phosphate-P concentrations ranged from 0 to 140 mg L^{-1} for the Zn-, Cu-, and Pb-saturated soils whereas they ranged from 0 to 40 mg L^{-1} for the Mn-, Ni-, and Cd-saturated soils.

The heavy metals released from metal-saturated soils to the matrix solution during equilibration of soil with the range of phosphate concentrations used to construct the adsorption isotherms were determined in the clear filtrate obtained to determine the P remaining in the

equilibrium solution. All metals were determined by atomic absorption spectrophotometry (Perkin-Elmer Model 5000).

RESULTS AND DISCUSSION

Phosphate adsorption by soils saturated with heavy metals was studied in three matrix solutions. The saturating metals examined were Mn, Ni, Cd, Cu, Zn, and Pb. According to Adriano et al. (1986) "heavy metal" refers to elements having densities >5.0, which is the case with all the metals used in this part of the study.

Phosphate adsorption was investigated by constructing adsorption isotherms by using a rather wide range of P concentration made in three matrix solutions, namely water, 0.01 M KCl, and 0.01 M $CaCl_2$. The results of phosphate adsorption by Mn-, Ni-, and Cd-saturated Hayden, Luther, Lester, Clarion, and Nicollet soils as affected by the matrix solution are shown in Figures 33-37. The corresponding results obtained for Cu-, Zn-, and Pb-saturated soils are shown in Figures 38-42 for Hayden, Luther, Lester, Clarion, and Nicollet soils, respectively. The isotherms of P adsorption by heavy metal-saturated soils are presented in two groups based on the workable range of P concentrations used.

Phosphate adsorption by Mn-, Ni-, and Cd-saturated soils as indicated by the location of adsorption isotherms was in the following order: Ni > Cd > Mn > untreated soil. This general trend was obtained for all soils, regardless of the type of matrix solution used. However, the amount of P adsorbed at any given equilibrium P concentration was the greatest when 0.01 M $CaCl_2$ was the matrix solution and the least when water was the matrix solution. Moreover, the amount of P adsorbed

Figure 33. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Hayden soil saturated with Mn, Ni, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

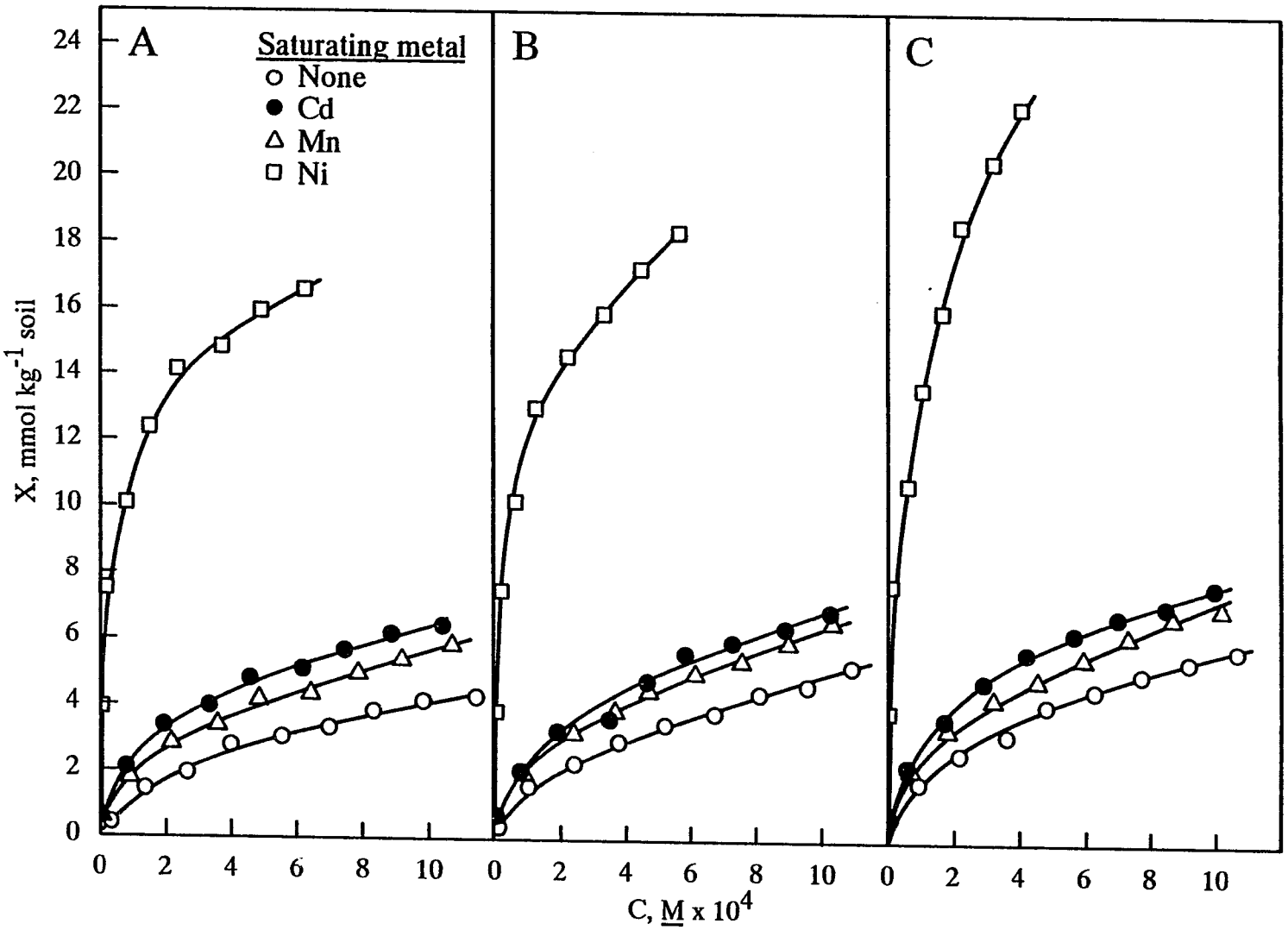

A
B
C
Saturating metal
None
Cd
Mn
Ni
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 34. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Luther soil saturated with Mn, Ni, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

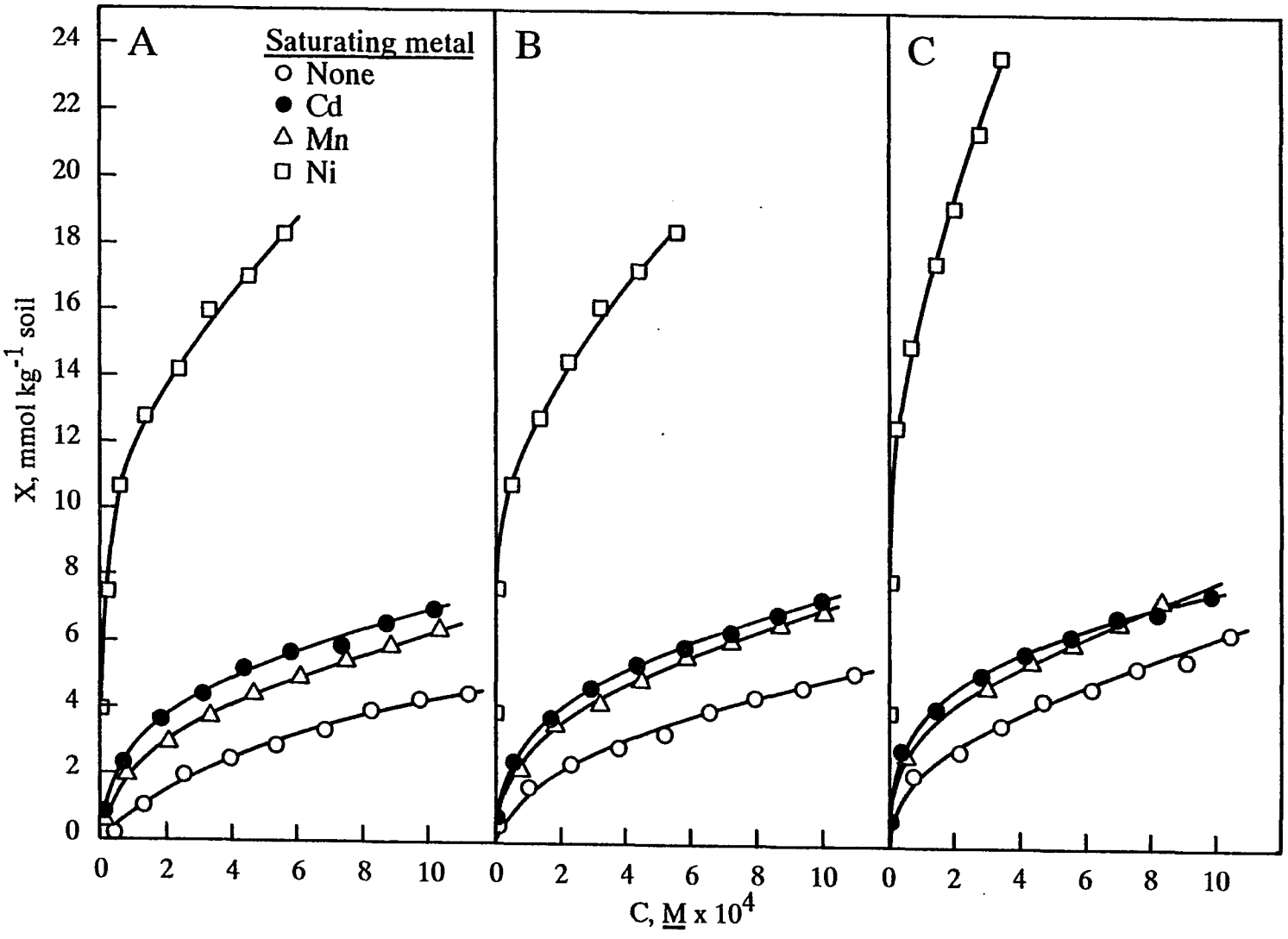

A
B
C
Saturating metal
None
Cd
Mn
Ni
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 35. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Lester soil saturated with Mn, Ni, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

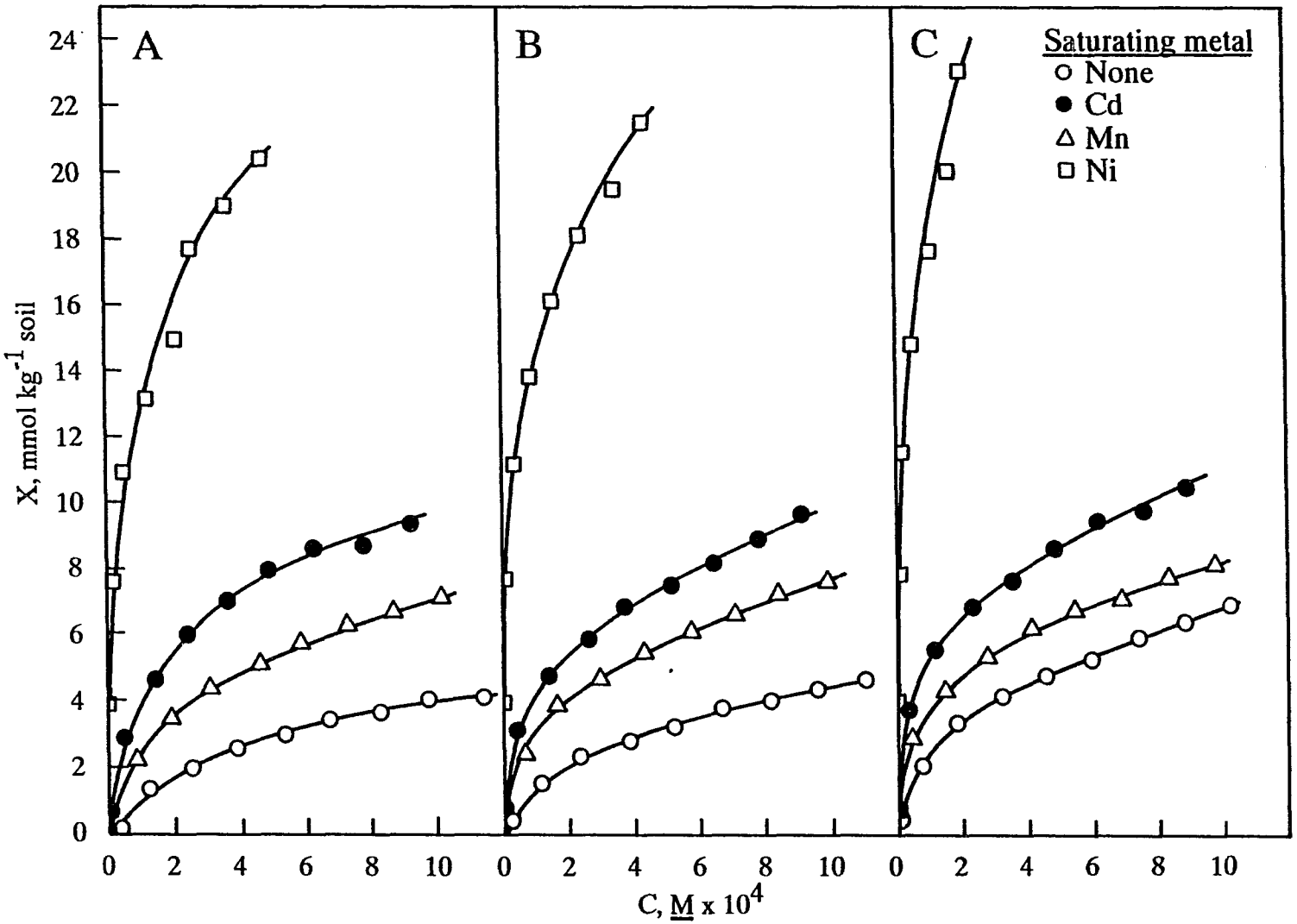

A
B
C
Saturating metal
None
Cd
Mn
Ni
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 36. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Clarion soil saturated with Mn, Ni, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

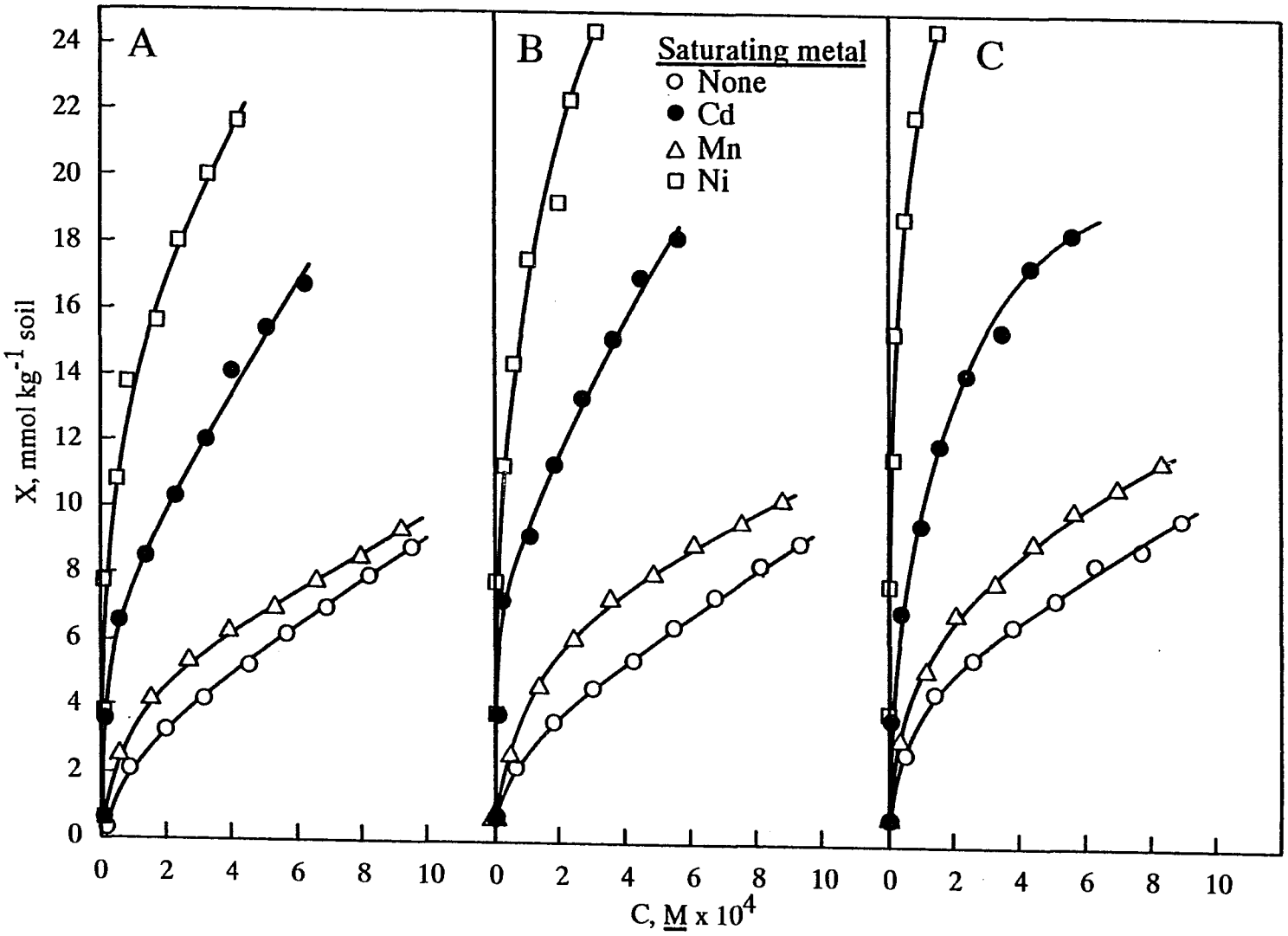

A
B
C
Saturating metal
None
Cd
Mn
Ni
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 37. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Nicollet soil saturated with Mn, Ni, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

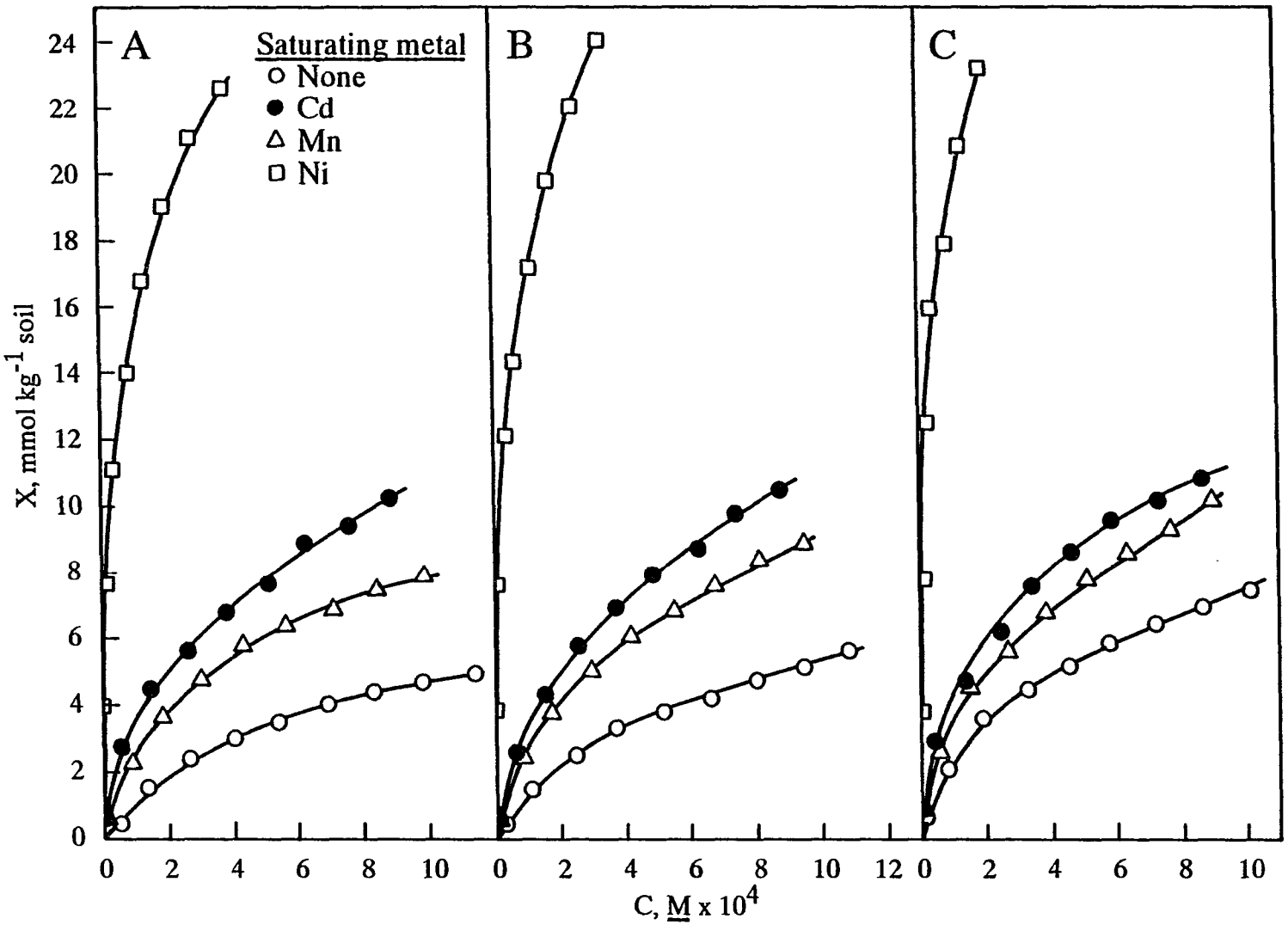

A
B
C
Saturating metal
None
Cd
Mn
Ni
X, mmol kg-1 soil
C, M x 10^4
0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 38. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Hayden soil saturated with Cu, Zn, or Pb as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

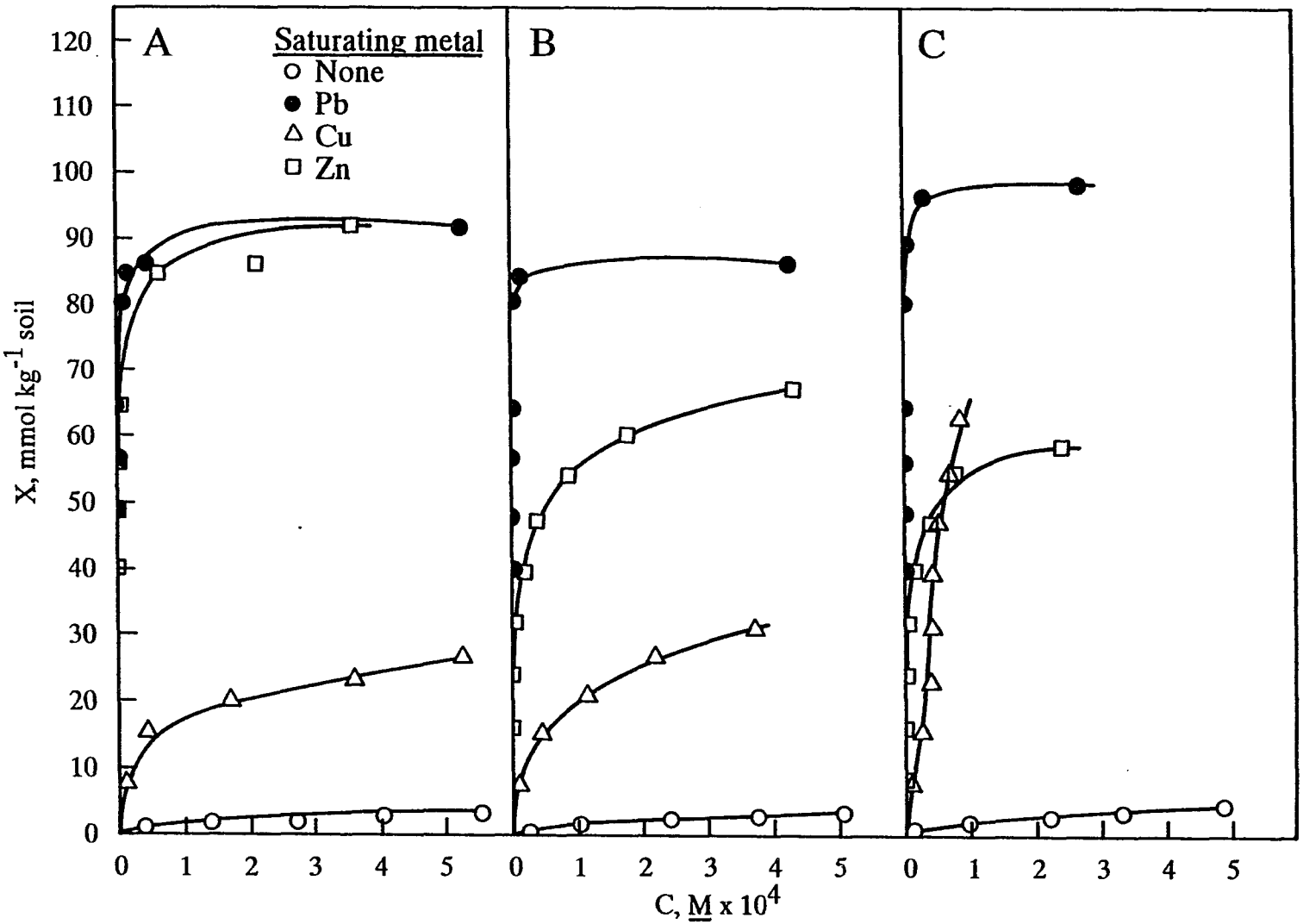

A
B
C
Saturating metal
None
Pb
Cu
Zn
X, mmol kg-1 soil
C, M x 10^4
0
10
20
30
40
50
60
70
80
90
100
110
120
0 1 2 3 4 5

Figure 39. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Luther soil saturated with Cu, Zn, or Pb as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

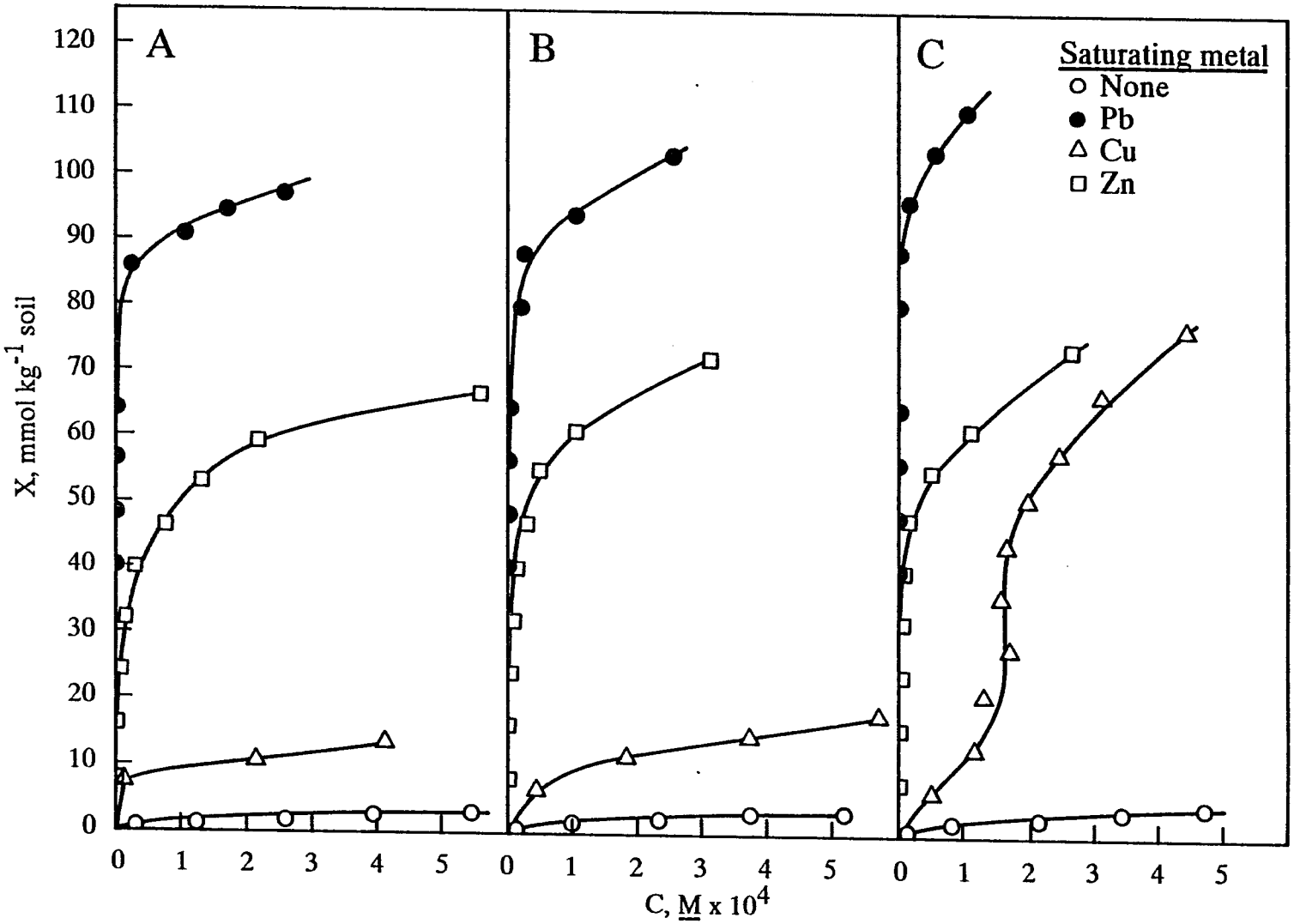

A
B
C
Saturating metal
None
Pb
Cu
Zn
X, mmol kg-1 soil
C, M x 10^4
0
10
20
30
40
50
60
70
80
90
100
110
120
0 1 2 3 4 5

Figure 40. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Lester soil saturated with Cu, Zn, or Pb as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

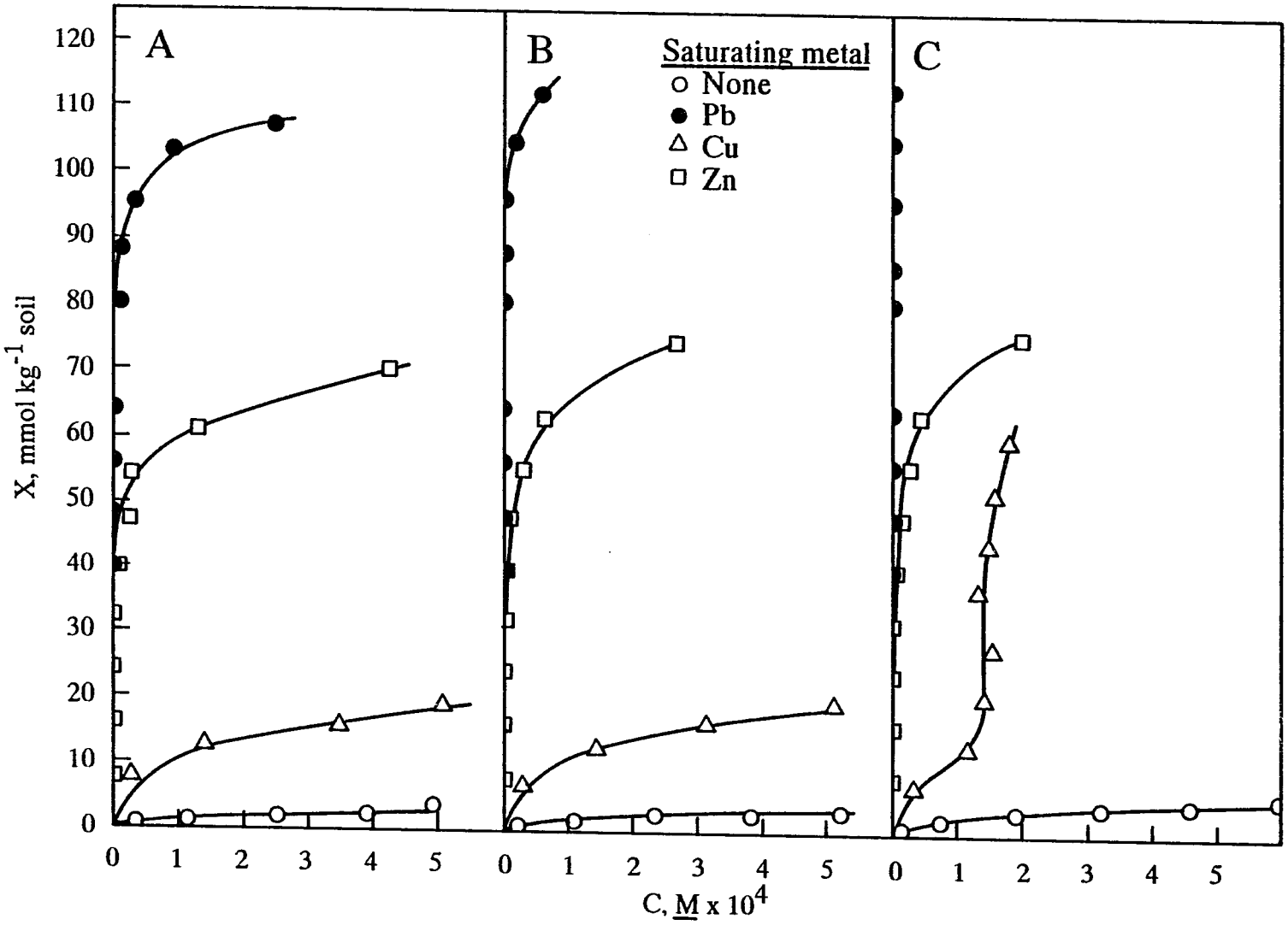

A
B
C
Saturating metal
None
Pb
Cu
Zn
X, mmol kg-1 soil
C, M x 10^4
0
10
20
30
40
50
60
70
80
90
100
110
120
0 1 2 3 4 5

Figure 41. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Clarion soil saturated with Cu, Zn, or Pb as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)

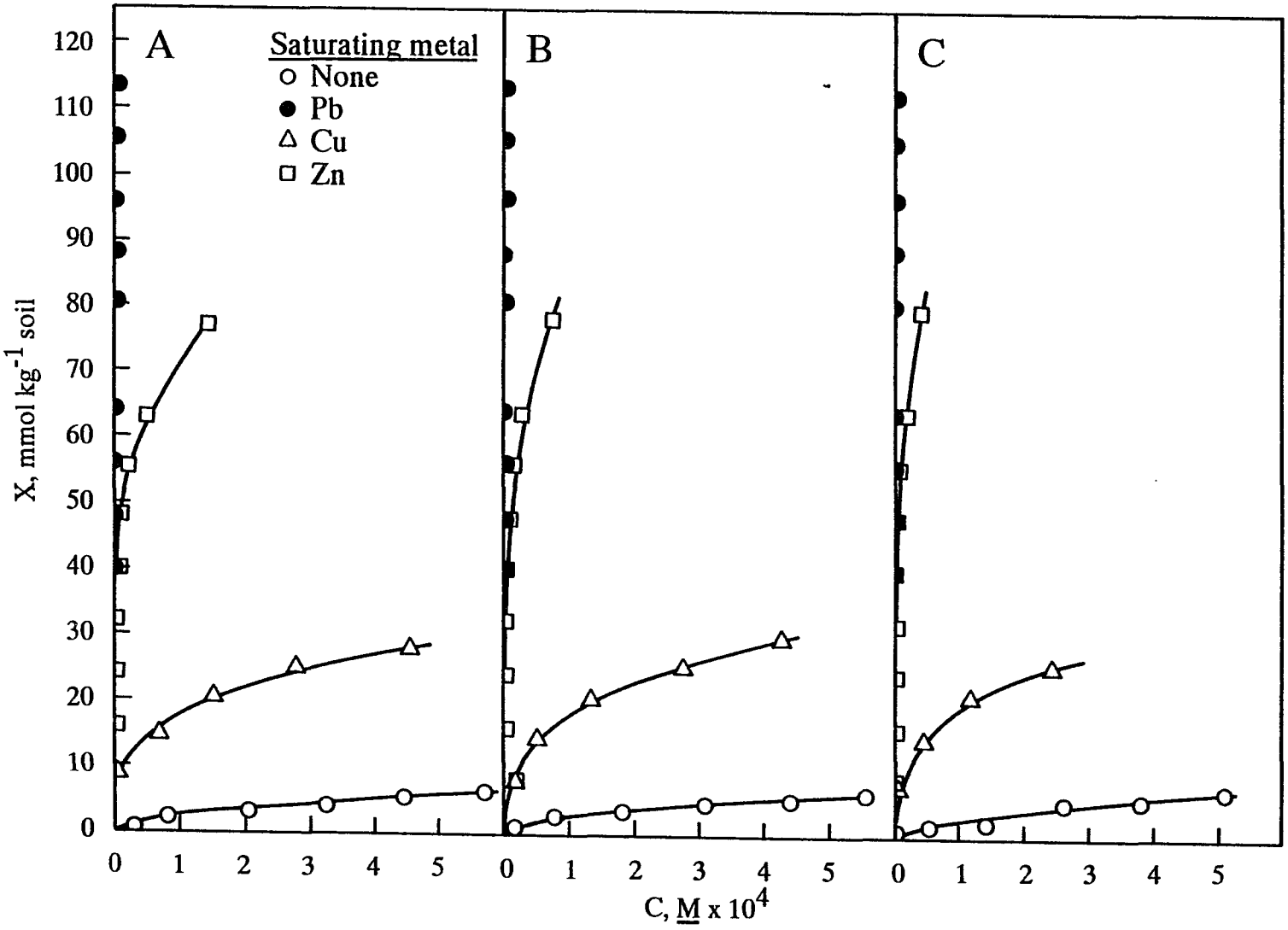
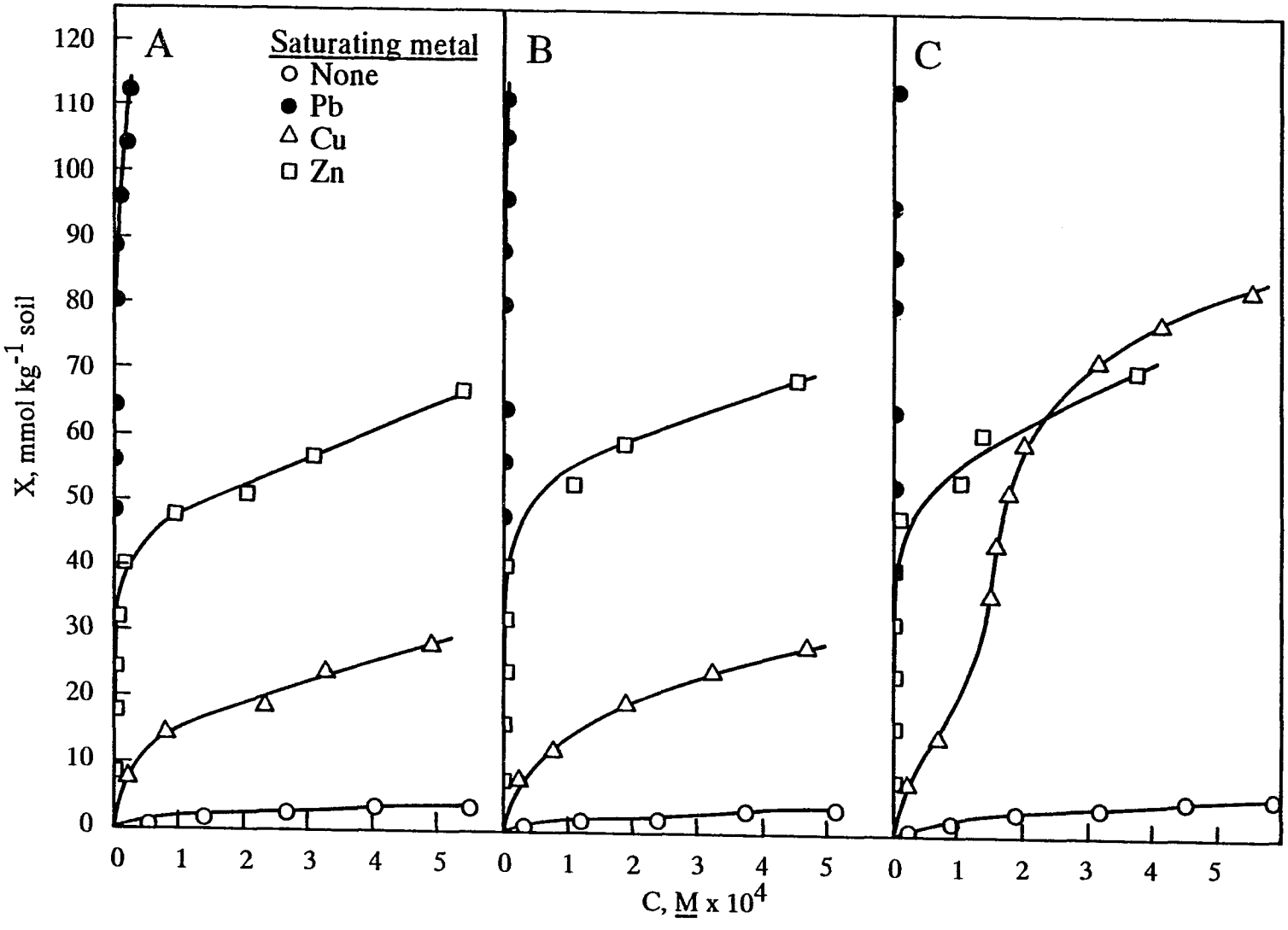

A
B
C
Saturating metal
None
Pb
Cu
Zn
X, mmol kg-1 soil
C, M x 10^4
0
10
20
30
40
50
60
70
80
90
100
110
120
0 1 2 3 4 5

Figure 42. The relationship between the amounts of phosphate-P adsorbed by soil (X) and the P concentration in the equilibrium solution (C) for Nicollet soil saturated with Cu, Zn, or Pb as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$)


A
B
C
Saturating metal
None
Pb
Cu
Zn
X, mmol kg-1 soil
C, M x 10^4
0
10
20
30
40
50
60
70
80
90
100
110
120
0 1 2 3 4 5

at any given equilibration P concentration differed with different soils.

Inspecting the shape of the adsorption isotherms (Figures 33-37) showed that the isotherms are either of H type (high affinity type), as in the case of Ni-saturated soils, or of L type (Langmuir type), as in the case of Cd- and Mn-saturated soils and untreated soils. Explanation of these two types of adsorption isotherms and their implication are given by Giles et al. (1960) and have been discussed in Part V.

Soils saturated with Ni exhibited a remarkable increase in P adsorption in comparison with saturation with either Cd or Mn and in comparison with untreated soil. This large increase in P adsorption obtained with soil saturated with Ni can be attributed to more than one reason. First, pH values of the Ni-saturated soils in the three matrix solutions (Table 27) were greater than the pH values of Mn- and Cd-saturated soils in any matrix solution. In fact, the pH values of Ni-saturated soils were >7.0, while the pH values of Mn- and Cd-saturated soils were <5.75, with a few exceptions. However, as indicated in Part II, the greatest P adsorption by soils was at pH >7 and the least was in pH values ranging from 5 to 6 (i.e., around zpc). Thus, the effect of Ni in increasing P adsorption may be partly due to its effect on the pH of soils. The second reason for the large increase in P adsorption by Ni-saturated soils is the efficiency of Ni in saturating the exchange sites. This is inferred from the amount of

Table 27. pH values of heavy metal-saturated soils as measured in various aqueous solutions

Soil	Heavy metal	pH of soil in aqueous solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
Hayden	None[b]	5.50	5.26	4.97
	Mn	5.40	5.36	5.23
	Ni	7.10	7.12	7.26
	Cu	5.41	5.51	5.50
	Zn	6.63	6.72	6.73
	Cd	5.14	5.15	5.12
	Pb	5.94	6.14	6.20
Luther	None	5.92	5.73	5.46
	Mn	5.73	5.63	5.53
	Ni	7.13	7.15	7.26
	Cu	5.20	5.25	5.18
	Zn	6.61	6.71	6.66
	Cd	5.37	5.35	5.39
	Pb	5.88	6.08	6.17
Lester	None	6.50	6.39	6.10
	Mn	6.17	6.14	5.97
	Ni	7.18	7.20	7.28
	Cu	5.07	5.15	5.12
	Zn	6.65	6.72	6.72
	Cd	5.72	5.81	5.79
	Pb	5.86	6.07	6.10
Clarion	None	5.80	5.70	5.36
	Mn	5.58	5.50	5.32
	Ni	7.04	7.07	7.05
	Cu	5.01	5.06	5.06
	Zn	6.51	6.62	6.58
	Cd	5.36	5.42	5.32
	Pb	5.82	5.98	6.00
Nicollet	None	6.03	5.84	5.52
	Mn	5.61	5.60	5.46
	Ni	7.04	7.03	7.06
	Cu	5.03	5.06	5.07
	Zn	6.55	6.57	6.54
	Cd	5.24	5.29	5.28
	Pb	5.85	5.99	6.02

[a,b]See footnotes of Table 20, Part V.

exchangeable Ni as determined by NH_4OAc in comparison with the amounts of Mn and Cd extracted from soils saturated with these metals (Table 28). The larger amount of Ni a soil retained may result in more efficient attraction of phosphate ions to the adsorption surfaces and therefore more P adsorption. Moreover, Ni is known to complex readily with a variety of organic ligands (Adriano, 1986). This high complexation of Ni with organic soil constituents may play an important role in the remarkable increase in P adsorption by Ni-saturated soils in comparison with P adsorption by Mn- or Cd-saturated soils.

Precipitation reaction of Ni with P was considered but excluded because of two reasons. First, analysis of Ni released to the equilibration solution showed that the amount of Ni released was relatively similar for the entire range of P concentrations used (Table 29). Second, the amounts of both Ni and P present in solution was below the concentration level investigated by Pratt et al. (1964) for the precipitation of either $6NiHPO_4.Ni(OH)_2.7H_2O$ or $4NiHPO_4.Ni_3(PO_4)_2.9H_2O$.

Phosphate adsorption isotherms for Cu-, Zn-, and Pb-saturated soils as affected by the matrix solution were presented in Figures 38-42. The amount of P adsorbed at any given equilibrium P concentration as indicated by the locations of the adsorption isotherms was in the following order: Pb-saturated soil > Zn-saturated soil > Cu-saturated soil > untreated soil. This trend of P adsorption was true for all soils regardless of the type of matrix solution used. It is noteworthy that the amount of P retained (adsorbed) by soils was calculated by

Table 28. Cation-exchange capacity of soils as determined by using NH_4OAc or heavy metal salt solutions

Saturation ion[b]	CEC of soil indicated[a]				
	Hayden	Luther	Lester	Clarion	Nicollet
	cmol (+) kg^- soil				
NH_4^+	10.5(100)	14.0(100)	19.5(100)	25.9(100)	25.8(100)
Mn^{2+}	11.0(105)	14.2(101)	19.0(97.4)	23.6(91.1)	23.1(89.5)
Ni^{2+}	23.7(226)	28.7(205)	38.2(196)	40.5(156)	44.3(172)
Cu^{2+}	26.5(252)	32.8(234)	46.3(237)	56.9(220)	63.2(245)
Zn^{2+}	20.9(199)	26.5(189)	32.1(165)	36.3(140)	38.4(149)
Cd^{2+}	11.7(111)	14.6(104)	23.1(119)	24.7(95.4)	27.4(106)
Pb^{2+}	22.0(210)	28.6(204)	39.2(201)	44.3(171)	42.4(164)

[a]Figures in parentheses are CEC values expressed as percentages of the values obtained by using neutral, 1 M NH_4OAc.

[b]For methods and procedures, see footnote of Table 17.

Table 29. Effect of matrix solutions used in constructing phosphate adsorption isotherms on the release of exchangeable metals from heavy metal-saturated soils

Soil	Heavy metal	Percentage of metal released to equilibrium solution specified[a]		
		Water	0.01 M KCl	0.01 M $CaCl_2$
		----------%[b]----------		
Hayden	Mn	22.3-29.1	47.0-55.9	76.0-80.5
	Ni	12.0-16.1	20.1-24.1	32.1-40.2
	Cu	3.46-8.80	7.74-15.6	7.65-19.8
	Zn	0.55-12.6	3.28-24.2	21.7-38.7
	Cd	20.5-27.1	49.3-54.2	77.3-85.5
	Pb	0.02-22.4	0.01-25.4	0.03-29.2
Luther	Mn	10.4-19.0	37.9-39.6	72.3-75.8
	Ni	13.4-16.7	20.1-25.0	44.8-59.9
	Cu	3.48-5.61	9.82-13.4	18.9-23.8
	Zn	1.01-9.70	2.86-20.6	21.4-34.9
	Cd	20.4-22.4	47.4-49.3	80.3-85.5
	Pb	0.069-14.1	0.023-16.6	0.087-20.4
Lester	Mn	5.20-9.10	25.8-28.5	69.9-75.0
	Ni	16.3-17.5	22.5-28.7	42.5-45.0
	Cu	4.96-7.41	8.92-12.7	16.8-20.2
	Zn	1.13-10.9	1.84-19.0	26.2-40.4
	Cd	17.5-20.8	34.2-37.1	70.8-79.2
	Pb	0.037-14.1	0.064-15.1	2.02-17.1
Clarion	Mn	7.30-12.5	29.2-34.3	66.5-74.8
	Ni	14.1-15.3	22.4-29.4	47.1-49.3
	Cu	4.84-8.28	10.5-13.4	16.9-21.4
	Zn	2.57-11.5	9.29-21.0	31.5-44.4
	Cd	15.8-17.7	33.4-34.6	66.0-70.8
	Pb	1.19-20.1	0.703-21.7	6.44-23.7
Nicollet	Mn	12.7-15.9	40.5-45.4	31.3-31.3
	Ni	17.2-18.3	24.7-26.9	40.9-43.1
	Cu	3.99-7.41	9.08-12.3	2.87-3.89
	Zn	0.46-0.68	7.87-18.0	4.19-9.59
	Cd	27.0-29.8	42.1-43.1	73.6-77.1
	Pb	0.174-15.5	0.168-18.5	0.038-8.72

[a]See footnote a of Table 22. For individual values, see Appendix Tables 41-46.

[b]See footnote b of Table 22.

subtracting the amount of P remained in the equilibrium solution from that initially added. However, when either Pb, Zn, or Cu was the saturating metal, precipitation reaction cannot be excluded even though the amount of P added was kept, in most cases, to the lowest workable concentration. Nevertheless, precipitation reaction is possible because an appreciable decrease in metal concentration was evident as the P concentration initially added increased (Table 29, Appendix Tables 43, 44, and 46). This is in agreement with the conclusions made by MacLean et al. (1969) and by Nriagu (1972, 1973a,b) that P may be used to alleviate the problem of soils contaminated with Pb. The large amounts of P retained by soils saturated with Pb, Cu, or Zn was necessitated by the use of a higher range of P concentrations than that used with other metals. The isotherms for P adsorption clearly indicate that, for all soils saturated with Pb, almost all the P added was retained. Also, the amount of Pb in the equilibrium solution decreased with increase in P addition. This may also support the conclusion made by Nriagu (1972, 1973a,b) regarding the importance of precipitation reaction along with adsorption reaction in retaining the added P by Pb-saturated soils.

The phosphate adsorption by heavy metal-saturated soils, as indicated by the locations of the adsorption isotherms, were in the following order: Pb > Zn > Cu > Ni > Cd > Mn > untreated soil (Table 30). Thus, the order of P adsorption by heavy metal-saturated soils and the amount of NH_4OAc extractable heavy metals were similar except in the case of Cu and Pb. The apparent exchangeable Cu was markedly

greater than the apparent exchangeable Pb in Cu- and Pb-saturated soils, respectively (Table 28). But the amounts of P adsorbed by Cu-saturated soils were less than those by Pb-saturated soils. This greater P adsorption by Pb-saturated soils suggests that reaction other than adsorption was involved when Pb was used as a saturating metal.

The large amounts of P adsorption by soils saturated with Cu, Pb, or Zn in comparison with the amounts adsorbed by the same soils but saturated with Cd, Mn, or Ni can be attributed to one of two reasons: (1) the amount of NH_4^+-exchangeable Pb, Cu, or Zn in their respective metal-saturated soils was three to four times greater than that of Cd, Mn, or Ni in their respective metal-saturated soils. Thus, the greatest amount of metals on the exchange sites can result in more efficient attraction of phosphate ions due to the decrease in surface negativity. (2) The larger amount of metal in soils may also interact with the organic soil constituents, consequently creating more P adsorption sites.

Phosphate adsorption isotherms of soils were also affected by the matrix solution used. Generally, P adsorption isotherms for Pb- and Zn-saturated soils, as affected by matrix solutions, were of the H type while that of Cu-saturated soils were of the L type when water and KCl were used as matrix solutions. The phosphate adsorption isotherms of the Cu-saturated soils were of S shape when $CaCl_2$ was the matrix solution (Figures 38-42). The H and L classes of adsorption isotherms were discussed before. The S shape of the adsorption isotherms is a special

case of L shape as discussed by Giles et al. (1960). For the initial slope of S curves, the more P adsorbed the easier it is for the additional amount of P to be adsorbed. This may in fact indicate that initially P reacts with Ca of the matrix solution to form uncharged ion pairs $(CaHPO_4)^o$ then followed by a sharp increase in amount of P adsorbed. This large increase in P adsorption may be attributed to the reaction of P (as HPO_4^{2-} or $H_2PO_4^-$) with the Cu^+ on the exchange sites and Cu^+ in the matrix solution. Another possible explanation is that the initial part of the S curves is due to P adsorption by soils where Cu^{2+} ions initiate the reaction by either forming an ion pair or positively charged molecules thus facilitating the P adsorption reactions. The first adsorbed molecules may behave as a nucleous for another reaction yet to develop. Again, the precipitation reaction may be the reason for the sharp increase in P retention in the second stage of adsorption isotherms. This explanation which involves adsorption followed by nucleation then precipitation was suggested by Griffen and Jurinak (1974), who indicated that precipitation reaction of P on $CaCO_3$ surface involves first adsorption, nucleation, then precipitation. They reported that, as precipitation proceeds, site coverage increases to the extent that lateral interaction occurs between the adsorbed ions. Lateral interaction produces doublets, triplets, and eventually surface clusters of P ions.

As it was discussed in Part II, the Langmuir equation is used to summarize the many results of adsorption isotherms in a few numbers.

The reasoning for using this model over the other models was also given in Part II. The Langmuir adsorption isotherms resulting from P adsorption by heavy metal-saturated Hayden and Clarion soils as affected by the matrix solution are shown in Figures 43 and 44, respectively. Similar plots were obtained for adsorption of P by the other three soils examined. These figures showed that plotting the data according to the Langmuir equation was effective in linearizing the data and further illustrating the effect of different heavy metals on P adsorption. The resulting values of X_m and k obtained by the Langmuir equation are presented in Table 30. The data clearly showed that the P adsorption maxima are varied depending on soil type, saturating metal, and matrix solution. However, the differences in X_m values were the greatest within one soil after saturation with a different metal. Also, saturating soils with heavy metals resulted in a marked increase in adsorption maxima. The general trend of X_m values calculated from the Langmuir model was as follows: Pb > Zn > Cu > Ni > Cd > Mn > untreated soil. This trend of decreasing X_m values was the same for all soils studied regardless of the matrix solution used.

The greatest X_m values of the heavy metal-saturated soil were obtained when $CaCl_2$ was used as a matrix solution. The least X_m values were not associated with a certain type of matrix solution, rather they varied with different soils and different saturating metals. For example, the X_m values of Hayden and Luther soils saturated with different metals were the greatest when $CaCl_2$ was the matrix solution

Figure 43. Langmuir isotherms for phosphate adsorption by Hayden soil saturated with Mn, Ni, Cu, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution

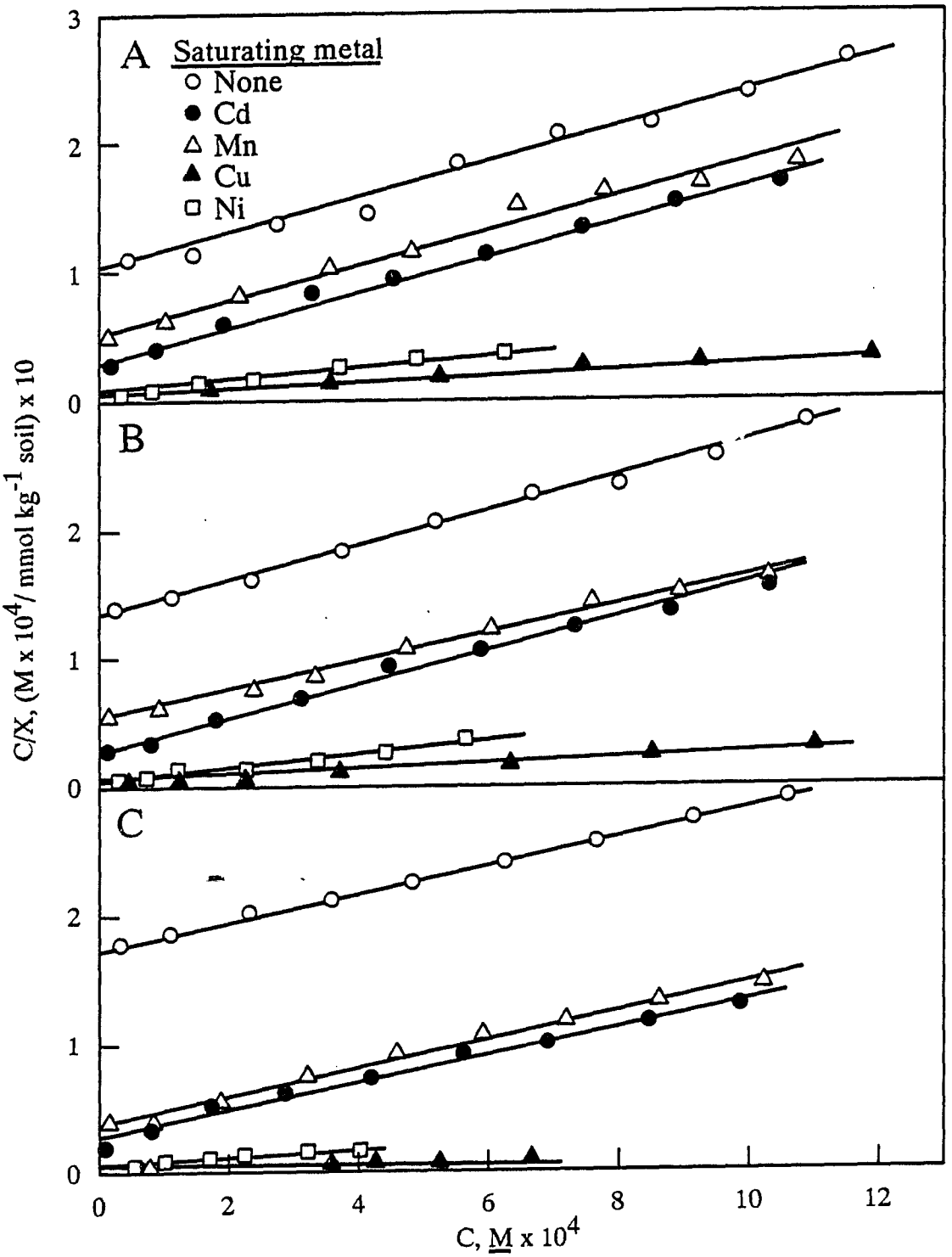

A Saturating metal
None
Cd
Mn
Cu
Ni
B
C
C/X, (M x 10^4/ mmol kg^-1 soil) x 10
C, M x 10^4
0
1
2
3
0
2
4
6
8
10
12

Figure 44. Langmuir isotherms for phosphate adsorption by Clarion soil saturated with Mn, Ni, Cu, or Cd as affected by the matrix solution (A, water; B, 0.01 M KCl; C, 0.01 M $CaCl_2$). Where (X) is the amount of phosphate-P adsorbed and (C) is the P concentration in the equilibrium solution

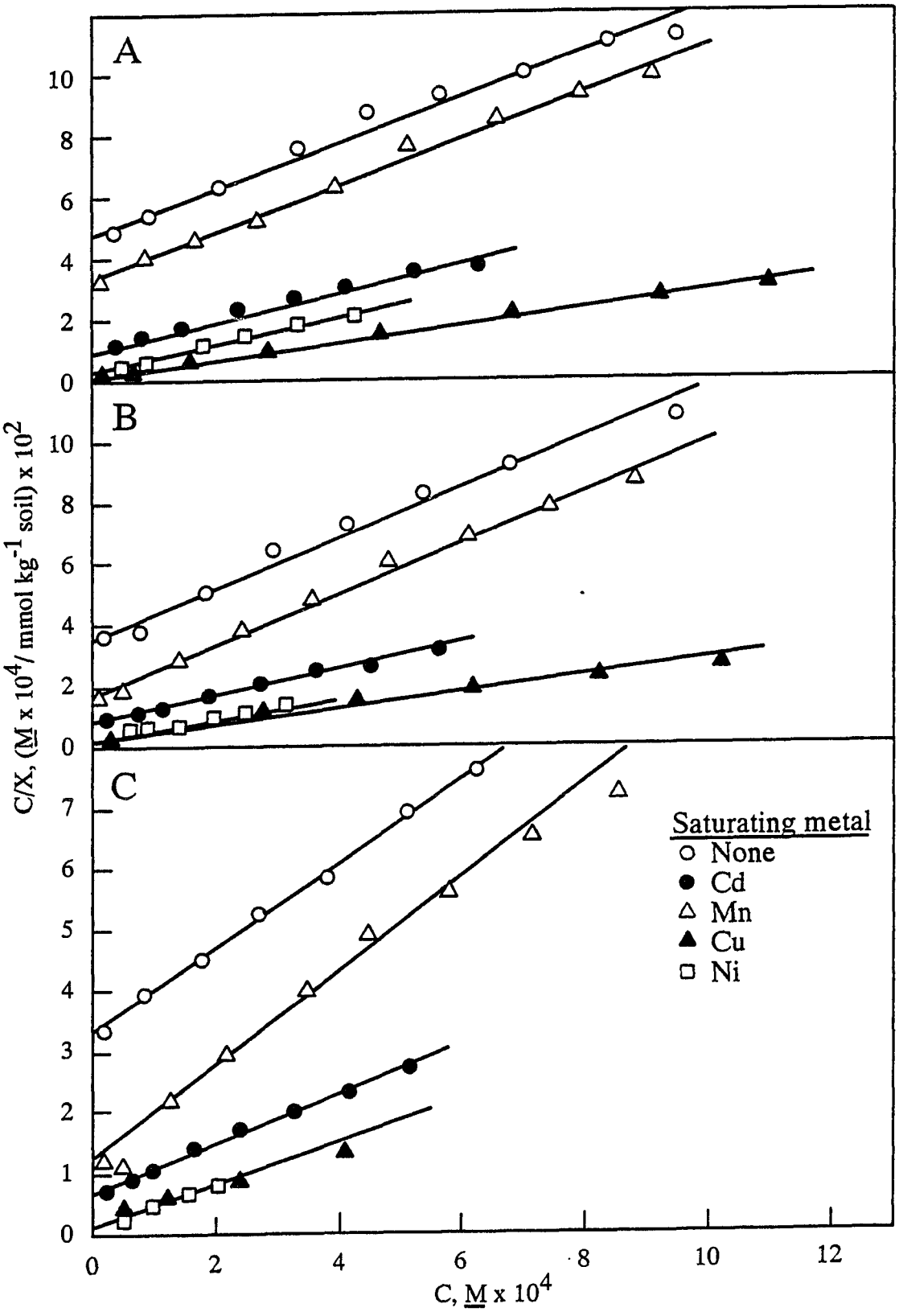

A
B
C
C/X, (M x 10^4 / mmol kg^-1 soil) x 10^2
C, M x 10^4
Saturating metal
None
Cd
Mn
Cu
Ni

Table 30. Langmuir constants for phosphate adsorption by heavy metal-saturated soils as affected by the equilibrium matrix solutions

Soil	Heavy metal	Water[a]		0.01 M KCl		0.01 M $CaCl_2$	
		X_m	k	X_m	k	X_m	k
Hayden	None[b]	6.77	1.52	7.41	1.71	9.71	1.39
	Mn	7.92	2.25	9.14	2.10	8.90	3.12
	Ni	16.9	29.5	20.0	25.0	24.1	20.7
	Cu	36.6	8.28	38.7	12.3	93.7	26.7
	Zn	91.7	178	69.1	54.8	65.9	58.4
	Cd	7.34	4.54	7.60	4.88	8.81	4.93
	Pb	91.5	102	92.4	78.0	97.6	8056
Luther	None	7.24	1.35	8.18	1.45	8.83	2.14
	Mn	9.54	1.84	9.93	2.19	10.9	2.42
	Ni	18.5	27.1	18.8	26.5	24.3	41.3
	Cu	30.3	2.07	30.3	2.75	96.5	8.63
	Zn	61.6	65.8	67.2	99.8	75.5	79.8
	Cd	8.69	3.60	9.09	3.55	8.96	4.87
	Pb	99.7	89.5	98.6	369	111	447
Lester	None	6.19	1.76	6.08	2.45	8.57	3.07
	Mn	9.71	2.58	9.60	3.26	9.80	4.44
	Ni	22.1	22.7	21.8	22.9	27.8	18.0
	Cu	29.0	4.93	32.6	0.99	100	24.9
	Zn	54.4	222	76.3	106	78.1	127
	Cd	10.8	5.81	10.2	7.54	10.6	8.57
	Pb	108	246	113	917	141	1185

Clarion	None	14.1	1.0	12.9	2.15	16.2	1.0
	Mn	13.5	2.25	12.3	4.79	12.9	5.92
	Ni	22.2	22.6	26.1	19.2	29.6	33.7
	Cu	38.1	8.76	42.3	7.88	37.6	13.3
	Zn	85.7	64.5	87.2	118	91.9	137
	Cd	22.1	4.52	24.6	5.08	24.8	5.71
	Pb	127	2809	140	1455	118	1269
Nicollet	None	7.07	1.86	7.23	2.13	10.0	2.56
	Mn	11.0	2.47	12.2	2.56	13.0	3.21
	Ni	23.7	21.1	27.7	18.0	29.1	17.2
	Cu	40.0	5.0	38.9	6.26	128	3.90
	Zn	67.3	32.8	70.2	59.8	71.9	75.2
	Cd	15.0	2.23	15.3	2.34	15.0	2.91
	Pb	118	461	148	724	118	1754

[a] X_m, adsorption maximum (mmol P kg^{-1} soil); k, affinity coefficient (reciprocal mmol L^{-1}) calculated from regression equations. All correlation coefficient values were >0.999 and were significant at $\underline{P}$ <0.01.

[b] None, natural (untreated) soil.

and the least when water was the matrix solution. The X_m values obtained for each untreated soil in the three matrix solutions were similar. This was also true for Mn-saturated soils; i.e., similar X_m values were obtained regardless of the matrix solution. On the other hand, the X_m values of the Ni-, Cu-, Zn-, and Pb-saturated soils were more variable; i.e., they were affected by the matrix solution used.

The k values were in the following order, regardless of the matrix solution used: Pb > Zn > Ni > Cu > Mn > Cd > untreated soil. Moreover, the k values of soils saturated with different metals were different with different matrix solutions. In general, the greatest k values of all metal-saturated soils were found when $CaCl_2$ was the matrix solution.

The results obtained in this part showed that, in addition to replacing the exchangeable cations in soils, treatment of soils with heavy metal will lead to formation of metal-organic complexes. This was evident from the results obtained when the heavy metal-saturated soils were extracted with NH_4OAc. Among the elements used, Mn and, to a certain extent, Cd formed less organic complexes than the other metals studied.

Phosphate adsorption was markedly affected by the saturating metal. Possible precipitation of phosphate with the metal released to the matrix solution was considered, and it was concluded that precipitation was possible only in the case of Cu, Zn, and Pb.

SUMMARY AND CONCLUSIONS

The major portion of phosphate fertilizer added to soils enters the solid phase as an adsorbed form. That is because of the high surface areas of soils and the rapidity of the adsorption reaction. Therefore, adsorption reaction is a very important mechanism controlling phosphate in soil solution and phosphate behavior in soils.

Phosphate adsorption is affected by numerous factors operating simultaneously. These factors include: pH, type and concentration of electrolytes, clay content, Al and Fe oxides, and organic matter content. Although the effects of most of these factors on phosphate adsorption by soils are relatively well known, the effect of exchangeable cations on phosphate adsorption by soils is not well understood, and in most cases it is overlooked. pH of the soil is the most important factor affecting the P adsorption by soils, but its effect in different soils is masked by the variation of other soil properties, therefore conflicting reports are found in literature on the effect of pH on P adsorption by soils.

Therefore, the objectives of this study were: (1) to develop a simple method for determination of surface charge density of soils; (2) to assess the effect of pH on phosphate adsorption by slightly acid soils; (3) to assess the effects of leaching with water and saturation with NH_4^+ on phosphate adsorption by soils; (4) to assess the effects of exchangeable alkali metals, alkaline earth metals, and selected heavy

metals on P adsorption by soils; and (5) to assess the effect of matrix solutions on phosphate adsorption by soils using kinetic models.

The results of this study can be summarized as follows:

1. A simple and precise method for determination of surface charge density of soils was developed. This method involves saturating the negative and positive exchange sites with NH_4^+ and NO_3^- ions, respectively, removing the excess solution by centrifugation, and determining the ions on the exchange sites by a steam distillation method. Results showed that the concentration and type of saturating ions and the extractants used significantly affected the surface negative charge densities. The average values of surface negative charge densities of 10 surface soils from Iowa, Chile, and Costa Rica by this method agreed closely with those obtained by the Schofield (1949) method [14.6 vs. 13.7 cmol (-) kg^{-1} soil]. The precision of the method for the results of replicated analysis of four soils showed that the averages for the negative charges ranged from 9.8 to 21.0 cmol (-) kg^{-1} soils, with standard deviations ranging from 0.34 to 0.68 and coefficients of variation ranging from 3.3 to 4.0. The averages of positive charges ranged from 1.0 to 4.0, with standard deviations ranging from 0.15 to 0.58 and coefficients of variation ranging from 10.1 to 16.6. The relatively high values of coefficients of variation exhibited by the positive charge densities of soils is related to the low values of this charge in soils. The advantages of the proposed method are no need for the laborious extraction steps and simplicity of the steam distillation method for determination of NH_4^+ and NO_3^- in soil samples.

2. Phosphate adsorption isotherms for all soils showed a distinct initial curvature, but no real saturation zone was found. The order of adsorption maxima obtained by employing the Langmuir model at different pH values differed from the order obtained from the locations on the plots of the P adsorption isotherms. This discrepancy was attributed to the slow reaction rates that followed the initial rapid adsorption reaction rate. Least affinity for P adsorption was found at the lowest pH (pH 4), whereas the greatest affinity was at pH 8.

Phosphate adsorption by soils from a constant amount of added P at a wide range of pH values showed that the minimum P adsorption by all soils was at a narrow zone of pH values (pH 4.5 to 5.5). Phosphate adsorption was sharply increased as the pH increased or decreased beyond this zone of minimum pH. The increase in P adsorption as the pH decreased below this minimum range of pH was attributed to the exchangeable Al and Al and Fe oxides. However, the increase in P adsorption with increase in pH above the minimum pH range was thought to be a result of exchangeable cation effects. This reasoning was confirmed when no increase in P adsorption was observed for the soils when the pH of the equilibration system was increased above the minimum value for the soils after the exchangeable cations were removed by saturation with NH_4^+ ions.

3. The greatest P adsorption by untreated, water-leached, or NH_4-saturated soils occurred when 0.01 M $CaCl_2$ was used as a matrix solution in comparison with when water or 0.01 M KCl was used as a matrix

solution. Phosphate adsorption by NH_4-saturated soils was the least as compared with that of the untreated or water-leached soils when water or KCl was used as a matrix solution, and the greatest when $CaCl_2$ was used as a matrix solution. Exchangeable Ca^{2+} rather than Ca^{2+} in solution played a major role in increasing P adsorption by soils as indicated by the large replacement (72-83%) of NH_4^+ on the exchange sites by Ca^{2+} ions provided by the matrix solution (0.01 M $CaCl_2$). Potassium ions were not as effective as Ca^{2+} in increasing P adsorption, although 51 to 84% of the NH_4^+ on the exchange sites were replaced by K^+ ions provided by the matrix solution (0.01 M KCl). Employing the Langmuir model, the results showed that the adsorption maximum (X_m) and the affinity coefficients (k) values for untreated, water-leached, or NH_4-saturated soils were the greatest when 0.01 M $CaCl_2$ was the matrix solution and the least when water was the matrix solution.

4. The amounts of P adsorbed by soils saturated with alkali metal were affected by the matrix solutions. The greatest amount of phosphate adsorption occurred when 0.01 M $CaCl_2$ was the matrix solution, and the least when water was the matrix solution. When water or 0.01 M KCl was used as a matrix solution, the amounts of P adsorbed by untreated soils were higher than those adsorbed by alkali metal-saturated soils (the least amount of P adsorption was exhibited by Na-saturated soils). When $CaCl_2$ was used as a matrix solution, the amounts of P adsorbed by the alkali metal-saturated soils followed the order: $K \geq Na > Rb > Cs > Li >$ untreated soil. Results also showed that the amounts of metals

released from alkali metal-saturated soils during equilibration of soils with P made in different matrix solutions were the least when water was the matrix solution and the greatest when 0.01 M $CaCl_2$ was the matrix solution. By employing the Langmuir model of P adsorption isotherms, results showed that the k values for soils saturated with alkali metal were the greatest when $CaCl_2$ was the matrix solution and the least when water was the matrix solution. This general trend was not observed for the X_m values.

5. The amount of P adsorbed by soils saturated with an alkaline earth metal at any given equilibrium P concentration was much higher than the amount adsorbed by the same soil but saturated with an alkali metal. The amounts of P adsorbed varied with matrix solution in the following order: $CaCl_2$ > KCl > water. In the three matrix solutions, the alkaline earth metal-saturated soils exhibited a general trend of P adsorption as follows: Ba-saturated soil > Ca-saturated soil > Mg-saturated soil > Sr-saturated soil > untreated soil. The amounts of these metals on the exchange sites, as determined by extraction with neutral, 1 M NH_4OAc, were in the same order as above for P adsorption by alkali earth metal-saturated soils. By employing the Langmuir model, the results showed that the X_m values of P adsorption by soils saturated with alkaline earth metal as affected by the matrix solution were in the following order: $CaCl_2$ > KCl > water. The possibility of precipitation of phosphate with the alkaline earth metals (Mg, Ca, Sr, or Ba) released to the matrix solution was considered but rejected because

calculation of the solubility of phosphates of these elements showed that, at the pH values of the soil-phosphate-matrix solution, these phosphates are soluble. Also the amounts of metals released to the matrix solution were not affected by the increase in phosphate concentration.

6. Phosphate adsorption by Mn-, Ni-, and Cd-saturated soils was in the following order: Ni > Cd > Mn > untreated soil, regardless of the type of matrix solution used. The amount of P adsorbed at any given equilibrium P concentration was the greatest when 0.01 M $CaCl_2$ was the matrix solution and the least when water was the matrix solution. Soils saturated with Ni exhibited a remarkable increase in P adsorption in comparison with Cd- or Mn-saturated soils. This was attributed to the high pH of the Ni-saturated soils and to the high efficiency of Ni in forming complexes with organic soil constituents. The amount of P adsorbed by Cu-, Zn-, and Pb-saturated soils at any given equilibrium P concentration was in the following order: Pb-saturated soil > Zn-saturated soil > Cu-saturated soil > untreated soil, regardless of the matrix solution used. When Pb, Zn, or Cu was the saturating metal, precipitation reaction was not excluded because an appreciable decrease in metal concentration was found as the P concentration initially added increased. For all soils saturated with Pb, almost all the P added was retained. In general, phosphate adsorption by heavy metal-saturated soils was in the following order: Pb > Cu > Zn > Ni > Cd > Mn > untreated soils. Different types of isotherms were obtained with

different metal saturation and with the different matrix solutions used. Employing the Langmuir model resulted in different X_m values, depending on soil, saturating metal, and the matrix solution used. The general trend of the X_m values for heavy metal-saturated soils was as follows: Pb > Zn > Cu > Ni > Cd > Mn > untreated soil. The k values for the same soils were in the following order, regardless of the matrix solution used: Pb > Zn > Ni > Cu > Mn > Cd > untreated soil.

The results reported showed that the minimum phosphate adsorption occurs at pH values ranging from 4.5 to 5.5, and that ammonium saturation of soils should greatly affect P adsorption. Although acid soils are limed to pH values near neutrality, apparently such practices minimize the efficiency of the added fertilizer P. Also, the results showed that application of P fertilizer with NH_4^+ or NH_4-forming fertilizers should increase the P fertilizer efficiency because results showed that saturating the soil exchange sites with NH_4^+ markedly decreased P retention. Other results showed that different alkali metals, alkaline earth metals, and heavy metals on the exchange sites have different effects on P adsorption by soils. This work also showed that P adsorption by soils is affected by type and amount of metals retained by soils (on the exchange sites or complexed with the organic soil constituents), and that adsorption isotherms are affected by equilibrium matrix solution used to construct P adsorption isotherms.

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APPENDIX

Table 31. Effect of matrix solutions on the amounts of NH_4^+ released from NH_4-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of NH_4^+ released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	24.9	23.7	75.8	72.2	86.6	82.5
	0.0323	26.6	25.3	74.5	71.9	87.2	83.1
	0.1614	27.9	26.6	76.1	72.5	87.6	83.4
	0.3228	33.8	33.0	75.1	71.5	89.2	85.8
	0.4843	32.5	31.0	75.1	71.5	84.3	80.3
	0.6457	38.0	36.3	76.8	73.1	86.9	82.8
	0.8071	38.4	36.6	85.9	81.8	84.3	80.3
	0.9685	42.3	40.3	88.6	84.1	83.3	79.3
	1.1300	44.3	42.2	83.0	79.1	85.3	81.2
	1.2914	45.3	43.1	86.9	82.8	87.6	83.4
Luther	0	27.9	19.9	86.8	63.3	107	76.4
	0.0323	29.8	21.3	88.2	63.0	105	75.0
	0.1614	32.5	23.2	94.1	67.2	105	75.0
	0.3228	38.4	27.4	92.5	66.0	105	75.0
	0.4843	42.0	30.0	87.2	62.2	106	75.7
	0.6457	42.0	30.0	87.6	62.6	107	76.4
	0.8071	42.0	30.0	88.6	63.3	106	75.7
	0.9685	47.9	34.2	89.9	64.2	105	75.0
	1.1300	44.3	31.6	88.6	63.3	107	76.4
	1.2914	48.9	34.9	89.9	64.2	104	74.3

Lester	0	56.7	29.1	113	57.9	153	78.5
	0.0323	44.3	22.7	103	52.8	138	70.8
	0.1614	47.6	24.4	106	54.4	143	73.3
	0.3228	47.6	24.4	115	59.0	149	76.4
	0.4843	47.9	24.6	118	60.5	149	76.4
	0.6457	54.4	27.9	118	60.5	149	76.4
	0.8071	51.8	26.6	123	63.1	146	74.9
	0.9685	58.7	30.1	117	60.0	149	76.4
	1.1300	63.3	32.5	117	60.0	151	77.4
	1.2914	66.6	34.2	118	60.5	148	75.9
Clarion	0	48.5	18.7	135	52.1	174	67.2
	0.0323	57.1	22.0	134	51.7	182	70.3
	0.1614	60.7	23.4	137	52.9	191	73.7
	0.3228	66.9	25.8	138	53.3	192	74.1
	0.4843	66.9	25.8	131	50.6	187	72.2
	0.6457	69.5	26.8	132	51.0	190	73.4
	0.8071	70.2	27.1	139	53.7	191	73.7
	0.9685	73.8	28.5	135	52.1	193	74.5
	1.1300	78.7	30.4	144	55.6	189	73.0
	1.2914	78.1	30.2	140	54.1	186	71.8
Nicollet	0	59.0	22.9	134	51.9	194	75.1
	0.0323	58.1	22.5	139	53.9	186	72.1
	0.1614	65.9	25.5	145	56.2	187	72.5
	0.3228	72.2	28.0	140	54.3	189	73.3
	0.4843	75.4	29.2	142	55.0	193	74.8
	0.6457	73.8	28.6	142	55.0	190	73.6
	0.8071	73.8	28.6	143	55.4	187	72.5
	0.9685	75.8	29.4	141	54.7	190	73.6
	1.1300	79.0	30.6	146	56.6	194	75.2
	1.2914	78.7	30.5	143	55.4	191	74.0

[a]Percentage of exchangeable NH_4^+ (Table 17).

Table 32. Effect of matrix solutions on the amounts of Li released from Li-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Li released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	21.6	30.0	72.0	100	81.0	113
	0.0323	21.6	30.0	68.4	95.0	81.0	113
	0.1614	23.4	32.5	68.4	95.0	75.6	105
	0.3228	28.8	40.0	79.2	110	81.0	113
	0.4843	35.3	49.0	64.8	90.0	79.2	110
	0.6457	36.0	50.0	86.4	120	81.0	113
	0.8071	41.4	57.5	72.0	100	93.6	130
	0.9685	37.8	52.5	72.0	100	82.8	115
	1.1300	50.4	70.0	70.2	97.5	79.2	110
	1.2914	55.8	77.5	75.6	105	90.8	126
Luther	0	35.3	40.9	95.4	110	112	130
	0.0323	39.6	45.8	91.8	106	108	125
	0.1614	35.3	40.9	90.0	104	110	127
	0.3228	46.8	54.2	93.6	108	105	122
	0.4843	46.8	54.2	97.2	113	109	126
	0.6457	46.8	54.2	91.8	106	110	127
	0.8071	46.1	53.4	91.8	106	103	119
	0.9685	48.6	56.3	93.6	108	105	121
	1.1300	54.0	62.5	91.8	106	108	125
	1.2914	55.1	63.8	99.0	114	110	127

Lester	0	46.1	35.7	119	92.2	144	112
	0.0323	46.1	35.7	115	89.1	148	115
	0.1614	54.0	41.9	116	89.9	141	109
	0.3228	59.4	46.0	117	90.7	141	109
	0.4843	55.8	43.3	115	89.1	141	109
	0.6457	64.8	50.2	116	89.9	126	97.7
	0.8071	69.2	53.6	116	89.9	137	106
	0.9685	79.2	61.4	119	92.2	142	110
	1.1300	72.0	55.8	114	88.4	144	112
	1.2914	81.0	62.8	121	93.8	119	92.2
Clarion	0	36.2	25.3	144	101	180	126
	0.0323	47.8	33.4	151	106	177	124
	0.1614	54.0	37.8	144	101	191	134
	0.3228	64.8	45.3	151	106	180	126
	0.4843	79.2	55.4	151	106	187	131
	0.6457	66.3	46.4	144	101	186	130
	0.8071	64.8	45.3	144	101	181	127
	0.9685	73.8	51.6	150	105	186	130
	1.1300	86.4	60.4	148	104	186	130
	1.2914	82.8	57.9	144	101	169	118
Nicollet	0	37.8	25.5	137	92.6	186	126
	0.0323	61.2	41.4	137	92.6	186	126
	0.1614	64.8	43.8	141	95.3	193	130
	0.3228	61.2	41.4	148	100	178	120
	0.4843	79.2	53.5	141	95.3	193	130
	0.6457	75.6	51.1	148	100	193	130
	0.8071	79.2	53.5	148	100	177	120
	0.9685	79.2	53.5	141	95.3	178	120
	1.1300	81.0	54.7	119	80.4	173	117
	1.2914	86.4	58.4	151	102	178	120

[a]Percentage of exchangeable Li (Table 17).

Table 33. Effect of matrix solutions on the amounts of Na released from Na-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Na released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	28.0	26.2	113	106	107	100
	0.0323	28.0	26.2	112	105	109	102
	0.1614	30.0	28.0	111	106	109	102
	0.3228	36.0	33.6	112	105	107	100
	0.4843	40.0	37.4	109	102	109	102
	0.6457	44.0	41.1	114	104	109	102
	0.8071	47.0	43.9	116	108	104	97.2
	0.9685	50.0	46.7	111	107	106	99.1
	1.1300	51.0	47.7	113	101	109	102
	1.2914	56.0	52.3	116	108	108	100
Luther	0	36.0	25.4	127	89.4	134	94.4
	0.0323	49.0	34.5	122	85.9	132	93.0
	0.1614	48.0	33.8	127	89.4	134	94.4
	0.3228	59.0	41.5	123	86.6	141	99.3
	0.4843	53.0	37.3	123	86.6	138	97.2
	0.6457	64.0	45.1	123	86.6	133	93.7
	0.8071	68.0	47.9	126	88.7	139	97.9
	0.9685	72.0	50.7	133	93.7	138	97.2
	1.1300	74.0	52.1	131	92.3	139	97.9
	1.2914	77.0	54.2	129	90.8	136	95.8

Lester	0	51.0	27.4	145	78.0	169	90.9
	0.0323	55.0	29.6	153	82.3	180	96.8
	0.1614	65.0	34.9	153	82.3	177	95.2
	0.3228	66.0	35.5	151	81.2	179	96.2
	0.4843	69.0	37.1	154	82.8	179	96.2
	0.6457	76.0	40.9	151	81.2	175	94.1
	0.8071	86.0	46.2	155	83.3	183	98.4
	0.9685	88.0	47.3	145	78.0	180	96.8
	1.1300	93.0	50.0	155	83.3	184	98.9
	1.2914	94.0	50.5	151	81.2	184	98.9
Clarion	0	50.0	21.2	182	77.1	205	86.9
	0.0323	52.0	22.0	177	75.0	203	86.0
	0.1614	54.0	22.9	182	77.1	211	89.4
	0.3228	59.0	25.0	178	75.4	206	87.3
	0.4843	66.0	28.0	176	74.6	214	90.7
	0.6457	68.0	28.8	181	76.7	199	84.3
	0.8071	89.0	37.7	178	75.4	208	88.1
	0.9685	76.0	32.2	178	75.4	213	90.3
	1.1300	86.0	36.4	179	75.8	209	88.6
	1.2914	90.0	38.1	183	77.5	213	90.3
Nicollet	0	92.0	36.7	208	82.9	226	90.0
	0.0323	91.0	36.3	201	80.1	226	90.0
	0.1614	99.0	39.4	214	85.3	222	88.4
	0.3228	102	40.6	211	84.1	230	91.6
	0.4843	102	40.6	203	80.9	226	90.0
	0.6457	107	42.6	214	85.3	236	94.0
	0.8071	113	45.0	227	90.4	232	92.4
	0.9685	111	44.2	218	86.9	221	88.0
	1.1300	113	45.0	222	88.4	240	95.6
	1.2914	120	47.8	205	81.7	227	90.4

[a]Percentage of exchangeable Na (Table 17).

Table 34. Effect of matrix solutions on the amounts of K released from K-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of K released in the presence of matrix solution specified			
		Water		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	27.0	24.5	86.0	78.2
	0.0323	29.0	26.4	80.0	72.7
	0.1614	33.0	30.0	90.0	81.8
	0.3228	39.0	35.5	97.0	88.2
	0.4843	39.0	35.5	102	92.7
	0.6457	45.0	40.9	102	92.7
	0.8071	50.0	45.5	102	92.7
	0.9685	51.0	46.4	103	93.6
	1.1300	56.0	50.9	106	96.4
	1.2914	61.0	55.5	102	92.7
Luther	0	32.0	26.0	112	91.1
	0.0323	32.0	26.0	108	87.8
	0.1614	35.0	28.5	110	89.4
	0.3228	42.0	34.1	105	85.4
	0.4843	42.0	34.1	109	88.6
	0.6457	51.0	41.5	110	89.4
	0.8071	58.0	47.2	103	83.7
	0.9685	58.0	47.2	105	85.4
	1.1300	63.0	51.2	108	87.8
	1.2914	68.0	55.3	110	89.4

Lester	0	45.0	24.9	228	126
	0.0323	47.0	26.0	169	93.4
	0.1614	47.0	26.0	166	91.7
	0.3228	56.0	30.9	166	91.7
	0.4843	61.0	33.7	173	95.6
	0.6457	69.0	38.1	184	102
	0.8071	71.0	39.2	176	97.2
	0.9685	79.0	43.6	181	100
	1.1300	79.0	43.6	186	103
	1.2914	86.0	47.5	200	111
Clarion	0	52.0	21.3	241	98.8
	0.0323	57.0	23.4	222	91.0
	0.1614	62.0	25.4	221	90.6
	0.3228	70.0	28.7	221	90.6
	0.4843	73.0	29.9	206	84.4
	0.6457	80.0	32.8	233	95.5
	0.8071	81.0	33.2	219	89.8
	0.9685	89.0	36.5	226	92.6
	1.1300	95.0	38.9	212	86.9
	1.2914	94.0	38.5	228	93.4
Nicollet	0	51.0	20.6	205	82.7
	0.0323	53.0	21.4	197	79.4
	0.1614	60.0	24.2	206	83.1
	0.3228	63.0	25.4	204	82.3
	0.4843	67.0	27.0	217	87.5
	0.6457	73.0	29.4	217	87.5
	0.8071	78.0	31.5	211	85.1
	0.9685	82.0	33.1	222	89.5
	1.1300	86.0	34.7	223	89.9
	1.2914	99.0	39.9	221	89.1

[a]Percentage of exchangeable K (Table 17).

Table 35. Effect of matrix solutions on the amounts of Rb released from Rb-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Rb released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	18.3	20.8	47.1	53.6	73.1	83.3
	0.0323	18.3	20.8	47.1	53.6	73.1	83.3
	0.1614	21.9	24.9	47.1	53.6	71.7	81.7
	0.3228	23.8	27.1	45.5	51.8	71.7	81.7
	0.4843	25.6	29.2	45.5	51.8	73.1	83.3
	0.6457	29.3	33.4	47.2	53.8	73.1	83.3
	0.8071	29.3	33.4	46.8	53.3	73.1	83.3
	0.9685	31.3	35.3	47.5	54.1	73.1	83.3
	1.1300	29.3	33.4	47.2	53.8	73.1	83.3
	1.2914	32.9	37.5	47.2	53.8	73.1	83.3
Luther	0	18.3	16.1	58.5	51.3	84.1	73.8
	0.0323	20.1	17.6	58.5	51.3	84.1	73.8
	0.1614	21.9	19.2	58.5	51.3	84.1	73.8
	0.3228	23.8	20.9	58.5	51.3	84.1	73.8
	0.4843	25.6	22.5	58.5	51.3	84.1	73.8
	0.6457	29.3	25.7	54.8	48.1	84.1	73.8
	0.8071	31.1	27.3	54.8	48.1	84.1	73.8
	0.9685	32.9	28.9	54.8	48.1	84.1	73.8
	1.1300	34.7	30.4	58.5	51.3	84.1	73.8
	1.2914	36.6	32.1	58.5	51.3	84.1	73.8

Lester	0	43.9	24.5	93.6	52.3	128	71.5
	0.0323	47.5	26.5	95.1	53.1	132	73.7
	0.1614	51.2	28.6	95.1	53.1	132	73.7
	0.3228	51.2	28.6	93.6	52.3	124	69.3
	0.4843	53.0	29.6	93.6	52.3	124	69.3
	0.6457	58.5	32.7	98.7	55.1	128	71.5
	0.8071	60.3	33.7	98.7	55.1	128	71.5
	0.9685	60.3	33.7	98.7	55.1	124	69.3
	1.1300	64.0	35.8	98.7	55.1	124	69.3
	1.2914	65.8	36.8	98.7	55.1	124	69.3
Clarion	0	34.7	14.2	91.1	37.2	139	56.7
	0.0323	40.2	16.4	88.5	36.1	139	56.7
	0.1614	42.0	17.1	87.6	35.8	139	56.7
	0.3228	43.9	17.9	89.1	36.4	139	56.7
	0.4843	45.7	18.7	86.8	35.4	139	56.7
	0.6457	47.5	19.4	87.6	35.8	139	56.7
	0.8071	49.4	20.2	89.3	36.4	140	57.1
	0.9685	51.2	20.9	88.4	36.1	140	57.1
	1.1300	51.2	20.9	89.2	36.4	140	57.1
	1.2914	53.0	21.6	89.0	36.3	140	57.1

[a]Percentage of exchangeable Rb (Table 17).

Table 36. Effect of matrix solutions on the amounts of Cs released from Cs-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Cs released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	11.3	19.3	65.2	111	51.5	87.9
	0.0323	13.9	23.7	63.3	108	52.3	89.3
	0.1614	14.6	24.9	60.0	102	52.9	90.3
	0.3228	15.3	26.1	58.7	100	51.7	88.2
	0.4843	16.2	27.8	60.9	104	53.7	91.6
	0.6457	19.1	32.7	62.3	106	54.0	92.2
	0.8071	20.2	34.5	64.9	111	51.0	87.0
	0.9685	22.9	39.1	60.2	103	57.3	97.8
	1.1300	24.3	41.5	61.6	105	52.7	89.9
	1.2914	23.9	40.8	66.2	113	52.6	89.8
Luther	0	5.6	6.34	65.9	74.6	69.3	78.6
	0.0323	6.4	7.21	64.4	72.9	56.9	64.4
	0.1614	10.7	12.1	65.0	73.5	59.9	67.8
	0.3228	12.1	13.7	65.5	74.1	61.2	69.2
	0.4843	14.3	16.2	66.8	75.6	64.3	72.7
	0.6457	16.4	18.6	68.2	77.2	62.0	70.1
	0.8071	17.6	19.9	67.9	76.8	64.4	72.9
	0.9685	20.6	23.3	69.1	78.2	63.9	72.3
	1.1300	22.2	25.1	66.9	75.7	63.9	72.3
	1.2914	24.0	72.2	68.5	77.5	64.2	72.6

Lester	0	17.6	12.0	96.0	65.3	106	72.1
	0.0323	15.0	10.2	96.7	65.8	109	74.1
	0.1614	21.5	14.6	95.8	65.2	102	69.4
	0.3228	24.3	16.5	102	69.4	108	73.5
	0.4843	27.7	18.8	104	70.7	109	74.1
	0.6457	31.9	21.7	108	73.5	110	74.8
	0.8071	34.5	23.5	106	72.1	109	74.1
	0.9685	40.4	27.5	107	72.8	113	76.9
	1.1300	44.6	30.3	104	70.7	108	73.5
	1.2914	43.4	29.5	105	71.4	110	74.8
Clarion	0	22.7	12.0	117	61.9	142	75.1
	0.0323	24.2	12.8	118	62.4	142	75.1
	0.1614	28.9	15.3	119	63.0	140	74.1
	0.3228	32.5	17.2	118	62.4	136	72.0
	0.4843	33.5	17.7	133	70.4	137	72.5
	0.6457	36.2	19.2	119	63.0	154	81.5
	0.8071	39.7	21.0	119	63.0	142	75.1
	0.9685	45.2	23.9	137	72.5	140	74.1
	1.1300	44.8	23.7	126	66.7	141	74.6
	1.2914	46.0	24.3	131	69.3	136	72.0
Nicollet	0	16.7	8.98	123	66.1	117	62.9
	0.0323	15.8	8.49	124	66.7	113	60.8
	0.1614	20.4	11.1	104	55.9	128	68.8
	0.3228	26.3	14.1	105	56.6	118	63.4
	0.4843	25.7	13.9	111	59.8	108	58.1
	0.6457	31.2	16.9	108	58.1	111	59.7
	0.8071	33.3	17.9	103	55.5	117	62.9
	0.9685	37.9	20.5	108	58.1	119	64.9
	1.1300	39.2	21.1	109	58.6	114	61.4
	1.2914	40.1	21.7	122	65.7	112	60.2

[a]Percentage of exchangeable Cs (Table 17).

Table 37. Effect of matrix solutions on the amounts of Mg released from Mg-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Mg released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	15.0	22.4	43.0	64.2	61.0	91.0
	0.0323	15.0	22.4	42.0	62.7	56.0	83.6
	0.1614	17.0	25.4	39.0	58.2	59.0	88.1
	0.3228	18.0	26.9	39.0	58.2	57.0	85.1
	0.4843	21.0	31.3	40.0	59.7	62.0	92.5
	0.6457	20.0	29.9	40.0	59.7	63.0	94.0
	0.8071	21.0	31.3	42.0	62.7	59.0	88.1
	0.9685	22.0	32.8	43.0	64.2	60.0	89.6
	1.1300	22.0	32.8	41.0	61.2	58.0	86.6
	1.2914	23.0	34.3	42.0	62.7	57.0	85.1
Luther	0	14.0	15.9	40.0	45.5	68.0	77.3
	0.0323	13.0	14.8	40.0	45.5	71.0	80.7
	0.1614	14.0	15.9	39.0	44.3	72.0	81.8
	0.3228	17.0	19.3	39.0	44.3	73.0	83.0
	0.4843	17.0	19.3	39.0	44.3	70.0	79.5
	0.6457	18.0	20.5	39.0	44.3	70.0	79.5
	0.8071	20.0	22.7	40.0	45.5	73.0	83.0
	0.9685	20.0	22.7	40.0	45.5	71.0	80.7
	1.1300	22.0	25.0	42.0	47.7	72.0	81.8
	1.2914	21.0	23.9	41.0	46.6	70.0	79.5

Lester	0	26.0	19.5	43.0	32.3	109	82.0
	0.0323	24.0	18.0	43.0	32.3	107	80.5
	0.1614	23.0	17.3	42.0	31.6	104	78.2
	0.3228	27.0	20.3	43.0	32.3	111	83.5
	0.4843	27.0	20.3	44.0	33.1	109	82.0
	0.6457	29.0	21.8	44.0	33.1	113	85.0
	0.8071	31.0	23.3	45.0	33.8	110	82.7
	0.9685	32.0	24.1	46.0	34.6	113	85.0
	1.1300	31.0	23.3	46.0	34.6	110	82.7
	1.2914	34.0	25.6	46.0	34.6	109	82.0
Clarion	0	24.0	15.7	52.0	34.0	124	81.0
	0.0323	26.0	17.0	52.0	34.0	125	81.7
	0.1614	25.0	16.3	52.0	34.0	126	82.4
	0.3228	27.0	17.6	50.0	32.7	123	80.4
	0.4843	28.0	18.3	52.0	34.0	123	80.4
	0.6457	27.0	17.6	50.0	32.7	122	79.7
	0.8071	30.0	19.6	53.0	34.6	123	80.4
	0.9685	30.0	19.6	53.0	34.6	121	79.1
	1.1300	30.0	19.6	53.0	34.6	122	79.7
	1.2914	32.0	20.9	55.0	35.9	122	79.7
Nicollet	0	28.0	18.4	62.0	40.8	124	81.6
	0.0323	27.0	17.8	59.0	38.8	121	79.6
	0.1614	29.0	19.1	57.0	37.5	124	81.6
	0.3228	29.0	19.1	60.0	39.5	123	80.9
	0.4843	30.0	19.7	59.0	38.8	123	80.9
	0.6457	31.0	20.4	61.0	40.1	121	79.6
	0.8071	32.0	21.1	60.0	39.5	120	78.9
	0.9685	32.0	21.1	62.0	40.8	124	81.6
	1.1300	33.0	21.7	61.0	40.1	123	80.9
	1.2914	34.0	22.4	64.0	42.1	122	80.3

[a]Percentage of exchangeable Mg (Table 23).

Table 38. Effect of matrix solutions on the amounts of Ca released from Ca-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Ca released in the presence of matrix solution specified			
		Water		0.01 M KCl	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	17.0	19.1	48.0	53.9
	0.0323	17.0	19.1	50.0	56.1
	0.1614	19.0	21.3	49.0	55.0
	0.3228	17.0	19.1	45.0	50.5
	0.4843	18.0	20.2	45.0	50.5
	0.6457	19.0	21.3	49.0	55.0
	0.8071	20.0	22.5	50.0	56.1
	0.9685	20.0	22.5	46.0	51.6
	1.1300	19.0	21.3	51.0	57.2
	1.2914	21.0	23.6	51.0	57.2
Luther	0	15.0	15.8	50.0	52.1
	0.0323	14.0	14.8	49.0	51.6
	0.1614	15.0	15.8	48.0	50.5
	0.3228	15.0	15.8	46.0	48.5
	0.4843	15.0	15.8	46.0	48.5
	0.6457	17.0	17.9	47.0	49.5
	0.8071	17.0	17.9	47.0	49.5
	0.9685	17.0	17.9	48.0	50.6
	1.1300	19.0	20.0	47.0	49.6
	1.2914	20.0	21.1	48.0	50.6

Lester	0	26.0	17.3	65.0	43.3
	0.0323	25.0	16.7	66.0	44.0
	0.1614	22.0	14.7	65.0	43.3
	0.3228	24.0	16.0	64.0	42.7
	0.4843	21.0	14.0	60.0	40.0
	0.6457	24.0	16.0	61.0	40.7
	0.8071	23.0	15.3	60.0	40.0
	0.9685	23.0	15.3	63.0	42.0
	1.1300	24.0	16.0	65.0	43.3
	1.2914	28.0	18.7	65.0	43.3
Clarion	0	28.0	15.6	93.0	52.0
	0.0323	24.0	13.4	89.0	49.7
	0.1614	28.0	15.6	87.0	48.6
	0.3228	26.0	14.5	89.0	49.7
	0.4843	26.0	14.5	88.0	49.2
	0.6457	27.0	15.1	87.0	48.6
	0.8071	28.0	15.6	85.0	47.5
	0.9685	30.0	16.8	88.0	49.2
	1.1300	36.0	20.1	88.0	49.2
	1.2914	36.0	20.1	90.0	50.3
Nicollet	0	26.0	14.1	76.0	41.3
	0.0323	28.0	15.2	78.0	42.4
	0.1614	28.0	15.2	73.0	39.1
	0.3228	27.0	14.7	72.0	39.1
	0.4843	28.0	15.2	75.0	40.8
	0.6457	28.0	15.2	74.0	40.2
	0.8071	28.0	15.2	72.0	39.1
	0.9685	30.0	16.3	73.0	39.8
	1.1300	28.0	15.2	72.0	39.1
	1.2914	28.0	15.2	70.0	38.0

[a]Percentage of exchangeable Ca (Table 23).

Table 39. Effect of matrix solutions on the amounts of Sr released from Sr-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Sr released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	14.8	27.5	28.6	53.2	35.2	65.4
	0.0323	15.4	28.6	30.5	56.7	43.7	81.2
	0.1614	12.1	22.5	29.7	55.2	44.8	83.3
	0.3228	15.1	28.1	27.2	50.6	50.0	92.9
	0.4843	14.6	27.1	29.9	55.6	46.7	86.8
	0.6457	14.8	27.5	28.0	52.0	47.5	88.3
	0.8071	15.9	29.6	28.0	52.0	46.1	85.7
	0.9685	15.4	28.6	28.6	53.2	49.2	91.4
	1.1300	15.7	29.2	27.7	51.5	46.4	86.2
	1.2914	16.5	30.7	29.7	55.2	45.6	84.8
Luther	0	7.97	10.5	26.6	35.1	54.7	72.2
	0.0323	6.32	8.30	27.2	35.9	54.4	71.8
	0.1614	7.14	9.40	26.9	35.5	55.2	72.8
	0.3228	9.06	12.0	28.0	36.9	53.6	70.7
	0.4843	9.06	12.0	26.9	35.5	56.0	73.9
	0.6457	8.51	11.2	26.4	34.8	56.6	74.7
	0.8071	9.89	13.0	27.2	35.9	53.8	71.0
	0.9685	10.7	14.1	27.5	36.3	56.3	74.3
	1.1300	10.7	14.1	26.6	35.1	56.6	74.7
	1.2914	10.7	14.1	29.1	38.4	51.4	67.8

Lester	0	15.1	12.3	28.3	23.0	82.4	67.0
	0.0323	12.4	10.1	28.8	23.4	81.9	66.6
	0.1614	11.8	9.60	28.3	23.0	83.5	67.9
	0.3228	11.0	8.90	27.5	22.4	84.0	68.3
	0.4843	11.5	9.3	28.6	23.3	82.9	67.4
	0.6457	13.5	11.0	28.3	23.0	84.6	68.8
	0.8071	12.4	10.1	28.3	23.0	82.4	67.0
	0.9685	14.3	11.6	28.8	23.4	83.5	67.9
	1.1300	14.8	12.0	27.5	22.4	84.6	68.8
	1.2914	14.0	11.4	30.2	24.6	85.1	69.2
Clarion	0	17.3	12.4	40.7	29.1	97.8	69.9
	0.0323	17.6	12.6	41.7	29.8	98.3	70.2
	0.1614	16.8	12.0	39.0	27.9	94.5	67.5
	0.3228	17.9	12.8	38.5	27.5	93.9	67.1
	0.4843	20.9	14.9	38.5	27.5	95.0	67.9
	0.6457	18.1	12.9	42.3	30.2	95.6	68.3
	0.8071	19.2	13.7	39.6	28.3	95.6	68.3
	0.9685	18.4	13.1	39.0	27.9	92.8	66.3
	1.1300	22.5	16.1	39.0	27.9	100	71.4
	1.2914	20.3	14.5	37.9	27.1	91.2	65.1
Nicollet	0	18.4	13.0	43.9	30.9	82.4	58.0
	0.0323	21.7	15.3	43.9	30.9	84.0	59.2
	0.1614	20.1	14.2	42.3	29.8	85.6	60.3
	0.3228	19.5	13.7	42.3	29.8	86.2	60.7
	0.4843	20.1	14.2	42.3	29.8	85.0	59.9
	0.6457	19.5	13.7	40.1	28.2	86.8	61.1
	0.8071	21.7	15.3	43.9	30.9	84.5	59.5
	0.9685	22.5	15.8	40.7	28.7	85.6	60.3
	1.1300	22.8	16.1	43.4	30.6	86.8	61.1
	1.2914	23.3	16.4	40.1	28.2	87.3	61.5

[a]Percentage of exchangeable Sr (Table 23).

Table 40. Effect of matrix solutions on the amounts of Ba released from Ba-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Ba released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	10.7	12.5	26.7	31.2	42.7	50.0
	0.0323	10.7	12.5	24.0	28.1	48.1	56.2
	0.1614	10.7	12.5	26.7	31.2	48.1	56.2
	0.3228	10.7	12.5	24.0	28.1	42.7	50.0
	0.4843	10.7	12.5	24.0	28.1	48.1	56.2
	0.6457	13.4	15.7	24.0	28.1	53.4	62.5
	0.8071	10.7	12.5	24.0	28.1	53.4	62.5
	0.9685	13.4	15.7	24.0	28.1	48.1	56.2
	1.1300	13.4	15.7	21.4	25.0	48.1	56.2
	1.2914	13.4	15.7	21.4	25.0	42.7	50.0
Luther	0	10.7	10.0	34.7	32.4	64.1	80.0
	0.0323	10.7	10.0	32.0	30.0	64.1	77.1
	0.1614	13.4	12.5	32.0	30.0	64.1	78.6
	0.3228	10.7	10.0	32.0	30.0	58.8	75.0
	0.4843	10.7	10.0	29.4	27.5	58.8	77.9
	0.6457	13.4	12.5	32.0	30.0	58.8	78.6
	0.8071	13.4	12.5	32.0	30.0	53.4	73.6
	0.9685	13.4	12.5	29.4	27.5	53.4	75.0
	1.1300	13.4	12.5	32.0	30.0	53.4	77.1
	1.2914	13.4	12.5	29.4	27.5	53.4	78.6

Lester	0	16.0	10.7	34.7	23.1	80.1	53.4
	0.0323	16.0	10.7	34.7	23.1	85.5	53.4
	0.1614	16.0	10.7	32.0	21.4	74.8	49.9
	0.3228	18.7	12.5	42.7	23.1	80.1	53.4
	0.4843	16.0	10.7	29.4	19.6	74.8	49.9
	0.6457	18.7	12.5	32.0	21.4	80.1	53.4
	0.8071	18.7	12.5	32.0	21.4	80.1	53.4
	0.9685	16.0	10.7	37.4	21.4	80.1	53.4
	1.1300	16.0	10.7	32.0	21.4	74.8	49.9
	1.2914	18.7	12.5	32.0	21.4	80.1	53.4
Clarion	0	24.0	14.1	48.1	25.0	90.8	53.1
	0.0323	24.0	14.1	42.7	25.0	90.8	53.1
	0.1614	24.0	14.1	42.7	25.0	96.1	56.2
	0.3228	24.0	14.1	42.7	25.0	96.1	56.2
	0.4843	21.4	12.5	42.7	25.0	90.8	53.1
	0.6457	21.4	12.5	37.4	21.9	90.8	53.1
	0.8071	21.4	12.5	42.7	25.0	96.1	56.2
	0.9685	24.0	14.1	37.4	21.9	85.5	50.0
	1.1300	24.0	14.1	37.4	21.9	85.5	50.0
	1.2914	24.0	14.1	37.4	21.9	85.5	50.0
Nicollet	0	21.4	25.0	45.4	26.6	80.1	53.4
	0.0323	21.4	25.0	42.7	25.0	85.5	53.4
	0.1614	18.7	21.9	37.4	21.9	74.8	49.9
	0.3228	18.7	21.9	40.1	23.4	80.1	53.4
	0.4843	18.7	21.9	42.7	25.0	74.8	49.9
	0.6457	18.7	21.9	42.7	25.0	80.1	53.4
	0.8071	18.7	21.9	40.1	23.4	80.1	53.4
	0.9685	18.7	21.9	40.1	23.4	80.1	53.4
	1.1300	18.7	21.9	37.4	21.9	74.8	49.9
	1.2914	21.4	25.0	37.4	21.9	80.1	53.4

[a]Percentage of exchangeable Ba (Table 23).

Table 41. Effect of matrix solutions on the amounts of Mn released from Mn-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Mn released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	12.3	22.3	30.7	55.9	41.7	76.0
	0.0323	12.3	22.4	28.2	51.4	41.7	76.0
	0.1614	13.5	24.6	25.8	47.0	41.7	76.0
	0.3228	12.3	22.4	28.2	51.4	44.2	80.5
	0.4843	12.3	22.4	28.2	51.4	41.7	76.0
	0.6457	12.3	22.4	28.2	51.4	44.2	80.5
	0.8071	13.5	24.6	29.5	53.7	44.2	80.5
	0.9685	16.0	29.1	28.2	51.4	44.2	80.5
	1.1300	13.5	24.6	28.2	51.4	44.2	80.5
	1.2914	14.7	26.8	27.0	49.2	44.2	80.5
Luther	0	7.4	10.4	28.2	39.6	54.0	75.8
	0.0323	7.4	10.4	28.2	39.6	51.5	72.3
	0.1614	7.4	10.4	28.2	39.6	51.5	72.3
	0.3228	7.4	10.4	28.2	39.6	51.5	72.3
	0.4843	8.6	12.1	28.2	39.6	51.5	72.3
	0.6457	8.6	12.1	27.0	37.9	54.0	75.8
	0.8071	8.6	12.1	29.5	41.4	51.5	72.3
	0.9685	9.8	13.8	27.0	37.9	51.5	72.3
	1.1300	13.5	19.0	27.0	37.9	54.0	75.8
	1.2914	11.1	15.6	28.2	39.6	51.5	72.3

Lester	0	7.40	7.80	25.8	27.2	71.2	75.0
	0.0323	4.90	5.20	25.8	27.2	68.7	72.4
	0.1614	4.90	5.20	24.5	25.8	68.7	72.4
	0.3228	4.90	5.20	25.8	27.2	68.7	72.4
	0.4843	7.40	7.80	25.8	27.2	68.7	72.4
	0.6457	7.40	7.80	25.8	27.2	68.7	72.4
	0.8071	6.10	6.40	25.4	26.8	66.3	69.9
	0.9685	7.40	7.80	25.8	27.2	68.7	72.4
	1.1300	8.60	9.10	27.0	28.5	68.7	72.4
	1.2914	8.60	9.10	27.0	28.5	71.2	75.0
Clarion	0	8.60	7.30	38.0	32.2	88.3	74.8
	0.0323	8.60	7.30	34.4	29.2	88.3	74.8
	0.1614	8.60	7.30	40.5	34.3	85.9	72.8
	0.3228	8.60	7.30	35.6	30.2	85.9	72.8
	0.4843	9.80	8.30	34.4	29.2	85.9	72.8
	0.6457	12.3	10.4	34.4	29.2	81.0	68.6
	0.8071	9.80	8.30	34.4	29.2	85.9	72.8
	0.9685	12.3	10.4	35.6	30.2	78.5	66.5
	1.1300	14.7	12.5	34.4	29.2	85.9	72.8
	1.2914	13.5	11.4	34.4	29.2	85.9	72.8
Nicollet	0	16.0	13.9	42.9	88.3	42.9	31.3
	0.0323	16.0	13.9	41.7	93.3	42.9	31.3
	0.1614	14.7	12.7	42.9	85.9	42.9	31.3
	0.3228	16.0	13.9	40.5	90.8	42.9	31.3
	0.4843	16.0	13.9	45.4	85.9	42.9	31.3
	0.6457	17.2	14.9	44.2	90.8	42.9	31.3
	0.8071	16.0	13.9	44.2	90.8	42.9	31.3
	0.9685	18.4	15.9	42.9	98.2	42.9	31.3
	1.1300	17.2	14.9	42.9	93.3	42.9	31.3
	1.2914	17.2	14.9	44.2	85.9	42.9	31.3

[a]Percentage of exchangeable Mn (Table 28).

Table 42. Effect of matrix solutions on the amounts of Ni released from Ni-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Ni released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	19.1	16.1	26.3	22.1	47.8	40.2
	0.0323	16.7	14.0	28.7	24.1	38.2	32.1
	0.1614	14.3	12.0	23.9	20.1	38.2	32.1
	0.3228	16.7	14.0	26.3	22.1	43.0	36.1
	0.4843	14.3	12.0	28.7	24.1	43.0	36.1
	0.6457	16.7	14.0	23.9	20.1	43.0	36.1
	0.8071	16.7	14.0	28.7	24.1	43.0	36.1
	0.9685	16.7	14.0	28.7	24.1	47.8	40.2
	1.1300	16.7	14.0	26.3	22.1	43.0	36.1
	1.2914	19.1	16.1	28.7	24.1	47.8	40.2
Luther	0	21.5	15.0	35.8	25.1	64.1	44.8
	0.0323	21.5	15.0	33.4	23.4	64.1	59.9
	0.1614	21.5	15.0	33.4	23.4	64.1	59.9
	0.3228	19.1	13.4	33.4	23.4	58.8	55.9
	0.4843	21.5	15.0	31.1	21.8	58.8	55.9
	0.6457	23.9	16.7	31.1	21.8	58.8	55.9
	0.8071	21.5	15.0	31.1	21.8	53.4	49.9
	0.9685	19.1	13.4	28.7	20.1	53.4	49.9
	1.1300	23.5	16.4	33.4	23.4	53.4	49.9
	1.2914	19.1	13.4	35.8	25.0	53.4	49.9

Lester	0	33.4	17.5	45.4	23.8	86.0	45.0
	0.0323	33.4	17.5	45.4	23.8	86.0	45.0
	0.1614	31.1	16.3	45.9	28.7	81.2	42.5
	0.3228	31.1	16.3	45.4	23.8	81.2	42.5
	0.4843	31.1	16.3	43.0	22.5	86.0	45.0
	0.6457	33.4	17.5	43.0	22.5	86.0	45.0
	0.8071	31.1	16.3	43.0	22.5	81.2	42.5
	0.9685	31.1	16.3	43.0	22.5	81.2	42.5
	1.1300	33.4	17.5	43.0	22.5	86.0	45.0
	1.2914	33.4	17.5	45.4	23.8	86.0	45.0
Clarion	0	28.7	14.1	54.9	27.0	95.6	47.1
	0.0323	28.7	14.1	45.4	22.4	95.6	47.1
	0.1614	28.7	14.1	50.2	24.7	95.6	47.1
	0.3228	28.7	14.1	59.7	29.4	100	49.3
	0.4843	28.7	14.1	45.4	22.4	95.6	47.1
	0.6457	31.1	15.3	47.8	23.5	95.6	47.1
	0.8071	28.7	14.1	45.4	22.4	95.6	47.1
	0.9685	31.1	15.3	45.4	22.4	95.6	47.1
	1.1300	28.7	14.1	47.8	23.5	95.6	47.1
	1.2914	28.7	14.1	45.4	22.4	100	49.3
Nicollet	0	40.6	18.3	59.7	26.9	95.6	43.0
	0.0323	38.2	17.2	59.7	26.9	95.6	43.1
	0.1614	40.6	18.3	59.7	26.9	100.0	45.1
	0.3228	38.2	17.2	57.3	25.8	90.8	40.9
	0.4843	35.8	16.1	54.9	24.7	95.6	43.1
	0.6457	40.6	18.3	54.9	24.7	95.6	43.1
	0.8071	38.2	17.2	54.9	24.7	95.6	43.1
	0.9685	40.6	18.3	54.9	24.7	100.0	45.1
	1.1300	40.6	18.3	54.9	24.7	95.6	43.1
	1.2914	40.6	18.3	54.9	24.7	95.6	43.1

[a]Percentage of exchangeable Ni (Table 28).

Table 43. Effect of matrix solutions on the amounts of Cu released from Cu-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Cu released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	10.3	7.74	17.2	12.0	26.4	19.9
	0.3228	11.7	8.80	20.7	15.1	33.7	11.8
	0.6457	9.60	7.22	19.7	14.8	32.1	11.5
	0.9685	7.80	5.86	17.9	13.5	31.2	11.5
	1.2910	7.80	5.86	14.7	11.1	28.9	10.1
	1.6140	4.60	3.46	13.8	10.5	26.4	9.26
	1.9370	4.60	3.46	13.8	10.5	25.6	8.98
	2.2600	4.60	3.46	12.6	9.77	26.4	9.26
	2.5830	4.60	3.46	12.6	9.45	25.6	8.98
	3.2280	4.60	3.46	11.5	8.81	25.6	8.98
	3.5510	4.60	3.46	11.5	8.71	25.6	8.98
	3.8740	4.60	3.46	10.3	7.73	25.6	8.98
	4.2000	5.70	4.29	10.3	7.72	22.9	8.04
	4.5200	5.70	4.29	10.3	7.72	21.8	7.65
Luther	0	6.90	4.21	18.4	11.2	31.0	18.9
	0.3228	9.60	5.85	23.2	14.2	37.9	23.1
	0.6457	9.20	5.61	22.9	14.0	39.0	23.8
	0.9685	8.50	5.18	21.3	13.8	37.9	23.1
	1.2910	8.70	5.30	22.0	13.4	38.1	23.2
	1.6140	5.70	3.48	19.5	11.9	35.6	21.7
	1.9370	5.70	3.48	18.4	11.2	36.7	22.4
	2.2600	5.70	3.48	18.4	11.2	36.7	22.4
	2.5830	5.70	3.48	18.4	11.2	36.7	22.4
	3.2280	6.90	4.21	19.5	11.8	36.7	22.4
	3.5510	6.90	4.21	20.7	12.6	36.7	22.4
	3.8740	8.00	4.88	18.4	11.2	34.4	21.0
	4.2000	8.00	4.88	16.1	9.82	35.6	21.7
	4.5200	8.00	4.88	17.2	10.5	34.1	21.0
Lester	0	13.8	5.95	25.2	10.8	41.3	17.8
	0.3228	17.2	7.41	29.4	12.7	46.6	20.1
	0.6457	15.8	6.81	26.6	11.5	46.8	20.2
	0.9685	15.1	6.51	26.2	11.3	45.4	19.6
	1.2910	14.5	6.25	25.2	10.9	45.7	19.7
	1.6140	11.5	4.96	21.8	9.40	39.0	16.8
	1.9370	11.5	4.96	20.7	8.92	40.2	17.3
	2.2600	11.5	4.96	20.7	8.92	40.2	17.3
	2.5830	11.5	4.96	20.7	8.92	39.0	16.8

	3.5510	6.90	4.21	20.7	12.6	36.7	22.4
	3.8740	8.00	4.88	18.4	11.2	34.4	21.0
	4.2000	8.00	4.88	16.1	9.82	35.6	21.7
	4.5200	8.00	4.88	17.2	10.5	34.1	21.0
Lester	0	13.8	5.95	25.2	10.8	41.3	17.8
	0.3228	17.2	7.41	29.4	12.7	46.6	20.1
	0.6457	15.8	6.81	26.6	11.5	46.8	20.2
	0.9685	15.1	6.51	26.2	11.3	45.4	19.6
	1.2910	14.5	6.25	25.2	10.9	45.7	19.7
	1.6140	11.5	4.96	21.8	9.40	39.0	16.8
	1.9370	11.5	4.96	20.7	8.92	40.2	17.3
	2.2600	11.5	4.96	20.7	8.92	40.2	17.3
	2.5830	11.5	4.96	20.7	8.92	39.0	16.8
	3.2280	11.5	4.96	20.7	8.92	41.3	17.8
	3.5510	11.5	4.96	20.7	8.92	40.2	17.3
	3.8740	11.5	4.96	21.8	9.40	39.0	16.8
	4.2000	13.8	5.95	25.2	10.9	41.3	17.8
	4.5200	11.5	4.96	21.8	9.40	40.2	17.3
Clarion	0	18.4	6.46	34.4	12.1	51.6	18.1
	0.3228	23.6	8.28	38.3	13.4	61.0	21.4
	0.6457	20.7	7.26	36.7	12.9	58.1	20.4
	0.9685	20.0	7.02	35.1	12.3	56.7	19.9
	1.2910	18.8	6.60	34.2	12.0	58.1	20.4
	1.6140	17.2	6.04	28.7	10.1	49.3	17.3
	1.9370	18.4	6.46	29.8	10.5	51.6	18.1
	2.2600	13.8	4.84	29.8	10.5	48.2	16.9
	2.5830	18.4	6.46	29.8	10.5	50.5	17.7
	3.2280	17.2	6.04	32.1	11.3	51.6	18.1
	3.5510	18.4	6.46	29.8	10.3	52.8	18.5
	3.8740	18.4	6.46	29.8	10.5	50.5	17.7
	4.2000	18.4	6.46	29.8	10.5	51.6	18.1
	4.5200	18.4	6.46	29.8	10.5	49.3	17.3
Nicollet	0	17.2	5.44	32.1	10.2	57.4	3.21
	0.3228	23.4	7.41	38.8	12.3	62.6	3.89
	0.6457	20.4	6.46	37.2	11.8	59.2	3.73
	0.9685	19.7	6.23	36.3	11.5	59.2	3.64
	1.2910	20.4	6.46	34.0	10.8	59.7	3.40
	1.6140	17.2	5.44	31.0	9.81	59.7	3.10
	1.9370	17.2	5.44	32.1	10.2	57.4	3.21
	2.2600	17.2	5.44	34.4	10.9	58.5	3.44
	2.5830	16.1	5.09	34.4	10.9	55.1	3.44
	3.2280	17.2	5.44	35.6	11.3	56.2	3.57
	3.5510	14.9	4.72	31.0	9.81	58.5	3.10
	3.8740	12.6	3.99	32.1	10.2	57.4	3.21
	4.2000	14.9	4.72	28.7	9.08	59.7	2.87
	4.5200	14.9	4.72	34.4	10.9	58.5	3.44

[a]Percentage of exchangeable Cu (Table 28).

Table 44. Effect of matrix solutions on the amounts of Zn released from Zn-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Zn released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	13.2	12.6	25.4	24.2	40.6	38.7
	1.6140	10.7	10.2	22.7	21.6	36.8	35.1
	1.9370	9.18	8.74	20.4	19.4	35.8	34.1
	2.2600	8.60	8.19	18.7	17.8	33.5	31.9
	2.5830	4.40	4.19	15.0	14.3	32.0	30.5
	3.2280	3.25	3.10	12.8	12.3	28.0	26.7
	3.5510	2.77	2.64	11.3	10.8	26.5	25.2
	3.8740	1.43	1.36	8.12	7.73	25.2	24.0
	4.2000	2.20	2.10	5.54	5.28	23.6	22.5
	4.5200	0.57	0.55	3.44	3.28	22.8	21.7
Luther	0	12.9	9.70	27.4	20.6	46.4	34.9
	1.6140	10.7	8.05	25.2	19.0	44.9	33.8
	1.9370	8.89	6.68	21.3	16.0	43.0	32.3
	2.2600	6.79	5.11	20.4	15.4	43.0	32.3
	2.5830	5.36	4.03	17.1	12.9	40.6	30.5
	3.2280	4.21	3.17	16.6	12.5	39.2	29.5
	3.5510	1.34	1.01	14.1	10.6	38.2	28.8
	3.8740	2.10	1.58	12.0	9.02	33.5	25.2
	4.2000	1.72	1.29	8.79	6.61	29.3	22.0
	4.5200	1.34	1.01	3.80	2.86	28.5	21.4

Lester	0	17.6	10.9	30.6	19.0	65.0	40.4
	1.6140	11.9	7.39	27.8	17.3	62.1	38.5
	1.9370	11.3	7.02	24.2	15.0	59.7	37.1
	2.2600	10.1	6.27	23.8	14.8	57.3	35.6
	2.5830	7.74	4.81	21.0	13.0	55.0	34.7
	3.2280	5.73	3.56	19.0	11.8	53.0	32.9
	3.5510	4.59	2.85	15.5	9.63	51.1	31.7
	3.8740	2.58	1.60	13.9	8.63	48.7	30.3
	4.2000	2.15	1.34	11.7	7.27	45.4	28.2
	4.5200	1.82	1.13	2.96	1.84	42.1	26.2
Clarion	0	20.9	11.5	38.2	21.0	80.8	44.4
	1.6140	17.9	9.84	33.5	18.4	77.9	42.8
	1.9370	17.1	9.40	32.0	17.6	74.6	41.0
	2.2600	15.3	8.41	31.5	17.3	70.7	38.9
	2.5830	13.5	7.42	28.1	15.4	71.7	39.4
	3.2280	11.3	6.21	27.2	15.0	71.7	39.4
	3.5510	8.98	4.93	24.3	13.7	68.3	37.5
	3.8740	7.84	4.31	22.8	12.5	64.5	35.4
	4.2000	5.07	2.79	20.5	11.3	61.2	33.6
	4.5200	4.68	2.57	16.9	9.29	57.3	31.5
Nicollet	0	18.2	9.68	33.9	18.0	74.1	9.59
	1.6140	16.3	8.67	33.9	18.0	68.8	9.59
	1.9370	15.2	8.09	33.0	17.6	71.2	9.34
	2.2600	15.4	8.19	32.0	17.0	63.6	9.05
	2.5830	12.6	6.70	28.2	15.0	64.0	7.98
	3.2280	10.7	5.69	24.6	13.1	64.0	6.96
	3.5510	8.03	4.27	24.2	12.9	64.0	6.85
	3.8740	6.50	3.46	23.2	12.3	60.2	6.56
	4.2000	3.44	1.83	19.8	10.5	61.2	5.60
	4.5200	0.86	0.46	14.8	7.87	49.2	4.19

[a]Percentage of exchangeable Zn (Table 28).

Table 45. Effect of matrix solutions on the amounts of Cd released from Cd-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Cd released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	13.0	22.2	31.8	54.2	48.2	82.2
	0.0323	13.0	22.2	30.8	52.6	50.1	85.5
	0.1614	15.9	27.1	28.9	49.3	45.3	77.3
	0.3228	14.0	23.8	29.9	51.0	46.2	78.9
	0.4843	12.0	20.5	29.9	51.0	47.2	80.5
	0.6457	14.4	24.7	31.8	54.2	48.2	82.2
	0.8071	14.0	23.8	31.8	54.2	49.1	83.8
	0.9685	14.4	24.7	31.8	54.2	49.1	83.8
	1.1300	15.9	27.1	31.8	54.2	49.1	83.8
	1.2914	15.9	27.1	31.8	54.2	47.2	80.5
Luther	0	14.9	20.4	36.1	49.3	61.6	84.2
	0.0323	14.9	20.4	34.7	47.4	61.6	84.2
	0.1614	14.9	20.4	35.2	48.1	60.7	82.9
	0.3228	15.4	21.0	34.1	46.6	59.7	81.6
	0.4843	15.4	21.0	35.2	48.1	62.6	85.5
	0.6457	16.4	22.4	35.2	48.1	61.6	84.2
	0.8071	14.9	20.4	34.2	46.7	60.7	82.9
	0.9685	14.9	20.4	35.6	48.6	58.8	80.3
	1.1300	16.4	22.4	36.1	49.3	62.6	85.5
	1.2914	15.9	21.7	36.1	49.3	60.7	82.9

Clarion	0	20.7	16.9	43.3	35.3	84.8	69.2
	0.0323	21.2	17.3	41.4	33.8	86.7	70.8
	0.1614	20.7	16.9	42.4	34.6	84.8	69.2
	0.3228	21.7	17.7	42.4	34.6	81.9	66.9
	0.4843	22.6	18.4	41.4	33.8	82.8	67.6
	0.6457	19.3	15.8	41.4	33.8	86.7	70.8
	0.8071	19.3	15.8	41.4	33.8	84.8	69.2
	0.9685	20.7	16.9	41.4	33.8	80.9	66.0
	1.1300	19.3	15.8	40.9	33.4	80.9	66.0
	1.2914	20.7	16.9	41.4	33.8	84.8	69.2
Nicollet	0	39.5	28.8	57.8	42.1	104	75.8
	0.0323	37.1	27.0	57.8	42.1	106	77.3
	0.1614	40.9	29.8	59.2	43.1	104	75.8
	0.3228	39.5	28.8	59.2	43.1	103	75.1
	0.4843	39.0	28.4	59.2	43.1	103	75.1
	0.6457	40.0	29.2	59.2	43.1	105	76.5
	0.8071	39.0	28.4	59.2	43.1	101	73.6
	0.9685	39.5	28.8	57.8	42.1	106	77.3
	1.1300	38.5	28.1	57.8	42.1	106	77.3
	1.2914	40.5	29.5	57.8	42.1	104	75.8
Lester	0	23.1	20.0	42.9	37.1	91.5	79.2
	0.0323	22.2	19.2	42.4	36.7	84.8	73.4
	0.1614	20.2	17.5	40.5	35.0	81.9	70.8
	0.3228	21.7	18.8	40.9	35.4	85.7	74.1
	0.4843	22.6	19.6	40.5	35.0	81.9	70.8
	0.6457	23.6	20.4	39.5	34.2	81.9	70.8
	0.8071	23.1	20.0	40.9	35.4	82.8	71.6
	0.9685	23.1	20.0	40.9	35.4	80.9	70.0
	1.1300	23.6	20.4	40.9	35.4	81.9	70.8
	1.2914	24.1	20.8	41.9	36.2	81.9	70.8

[a]Percentage of exchangeable Cd (Table 28).

Table 46. Effect of matrix solutions on the amounts of Pb released from Pb-saturated soils after equilibration with various concentrations of phosphate-P at 25°C for 24 h

Soil	Initial P conc.	Amount of Pb released in the presence of matrix solution specified					
		Water		0.01 M KCl		0.01 M $CaCl_2$	
	mM	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]	mmol kg^{-1}	%[a]
Hayden	0	24.6	22.4	28.0	25.5	32.1	29.2
	1.6140	11.2	10.2	12.4	11.3	18.6	16.9
	1.9370	6.76	6.15	7.42	6.74	15.5	14.1
	2.2600	3.46	3.15	4.45	4.045	10.4	9.46
	2.5830	1.29	1.17	2.47	2.245	10.1	9.18
	3.2280	0.349	0.32	0.145	0.132	8.42	7.66
	3.5510	0.033	0.030	0.020	0.018	0.297	0.270
	3.8740	0.020	0.018	0.013	0.012	0.079	0.072
	4.2000	0.013	0.012	0.007	0.006	0.040	0.036
	4.5200	0.020	0.018	0.007	0.006	0.033	0.030
Luther	0	20.1	14.1	23.7	16.6	29.2	20.4
	1.6140	6.92	4.84	8.41	5.88	14.7	10.2
	1.9370	3.79	2.65	6.59	4.61	13.7	9.58
	2.2600	1.92	1.34	4.78	3.34	11.0	7.69
	2.5830	1.46	1.02	0.158	0.110	10.2	7.13
	3.2280	0.191	0.134	0.119	0.083	3.30	2.30
	3.5510	0.073	0.051	0.059	0.041	3.13	2.18
	3.8740	0.033	0.023	0.033	0.023	0.725	0.507
	4.2000	0.125	0.087	0.105	0.073	0.211	0.148
	4.5200	0.099	0.069	0.145	0.101	0.125	0.087

Lester	0	27.7	14.1	29.5	15.1	33.5	17.1
	1.6140	10.7	5.46	11.4	5.82	24.7	12.6
	1.9370	9.07	4.63	11.0	5.61	20.9	10.7
	2.2600	2.97	1.52	6.59	3.36	16.0	8.2
	2.5830	2.47	1.26	3.96	2.02	25.4	13.0
	3.2280	0.290	0.148	1.07	0.546	15.7	8.01
	3.5510	0.303	0.155	0.389	0.198	11.0	5.61
	3.8740	0.132	0.067	0.125	0.064	9.23	4.71
	4.2000	0.059	0.030	0.231	0.118	3.96	2.82
	4.5200	0.073	0.037	0.666	0.340	5.27	2.69
Clarion	0	44.5	20.1	48.1	21.7	52.6	23.7
	1.6140	30.5	13.7	28.7	12.9	39.6	17.8
	1.9370	26.4	11.9	27.4	12.3	36.8	16.6
	2.2600	23.6	10.6	23.2	10.5	34.9	15.7
	2.5830	18.3	8.24	20.9	9.41	31.5	14.2
	3.2280	17.6	7.93	14.5	6.53	27.7	12.5
	3.5510	15.2	6.85	14.5	6.53	28.2	12.7
	3.8740	16.0	7.25	12.9	5.81	23.6	10.6
	4.2000	6.76	3.05	5.600	2.52	30.0	13.5
	4.5200	2.64	1.19	1.560	0.703	14.3	6.44
Nicollet	0	32.8	15.5	39.2	18.6	43.0	8.72
	1.6140	18.3	8.63	17.5	8.26	28.2	3.89
	1.9370	12.7	5.99	14.8	6.98	27.5	3.29
	2.2600	5.9	2.80	12.5	5.90	25.9	2.78
	2.5830	10.2	4.81	9.89	4.67	23.4	2.20
	3.2280	3.96	1.81	7.09	3.34	24.6	1.58
	3.5510	0.481	0.227	1.81	0.854	15.7	0.403
	3.8740	1.37	0.666	1.69	0.797	17.6	0.376
	4.2000	0.369	0.174	0.692	0.326	7.58	0.154
	4.5200	0.534	0.252	0.356	0.168	4.12	0.079

[a]Percentage of exchangeable Pb (Table 28).